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

$L$S-coupling:  Foot 5

Detailed energy structure within a configuration
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

\( \delta \) is:
- experimentally determined
- strongly dependent of \( \ell \)
- approximately independent of \( n \).
Energy scales (Values for H)

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

Diagram showing energy levels and term values for H.
Term values in Li and H.

\[ T = E_{\text{ion}} - E \]

<table>
<thead>
<tr>
<th>$T_{\exp}$ / cm(^{-1})</th>
<th>$T_H = \frac{1}{3^2} R_{\text{Li}}$ / cm(^{-1})</th>
<th>% deviation</th>
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<tbody>
<tr>
<td>$1s^23s$ 16281</td>
<td>12192</td>
<td>33</td>
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<tr>
<td>$1s^23p$ 12562</td>
<td>-&quot;-</td>
<td>3</td>
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<tr>
<td>$1s^23d$ 12204</td>
<td>-&quot;-</td>
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Electrons with $\ell > 0$ are "pushed outwards by the centrifugal force"
Penetrating orbitals in Na
(Foot Fig 4.1)

(a)

Core 1s²2s²2p⁶

3s

(b)

Core 1s²2s²2p⁶

3p

(c)

Core 1s²2s²2p⁶

3d
Quantum defect in F VII

\[ T = R \cdot \frac{Z^2}{n^2} \quad \text{H-like} \]

\[ T = R \cdot \frac{\zeta^2}{n^2} \quad \text{Completely screened nucleus} \]

\[ \zeta = Z - N_{\text{iner}} \]

\[ T = R \cdot \frac{\zeta^2}{(n - \delta)^2} \quad \delta = \text{quantum defect} \]

\[ \delta \text{ is:} \]
- experimentally determined
- strongly dependent of \( \ell \)
- approximately independent of \( n \).

Quantum defect in F VII (Li-like)

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<tr>
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<th>( s )</th>
<th>( p )</th>
<th>( d )</th>
<th>( f )</th>
<th>( g )</th>
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</table>

Na-spectrum

- 3p-5d 4982.8
- 3p-4d 5687.9
- 3s-3p 5893.6
- 3p-5s 6160.3
- 3p-7d 4497.8
- 3p-6d 4668.6

Wavelength / Å

Intensity
Fine structure in the alkalis

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

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

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

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