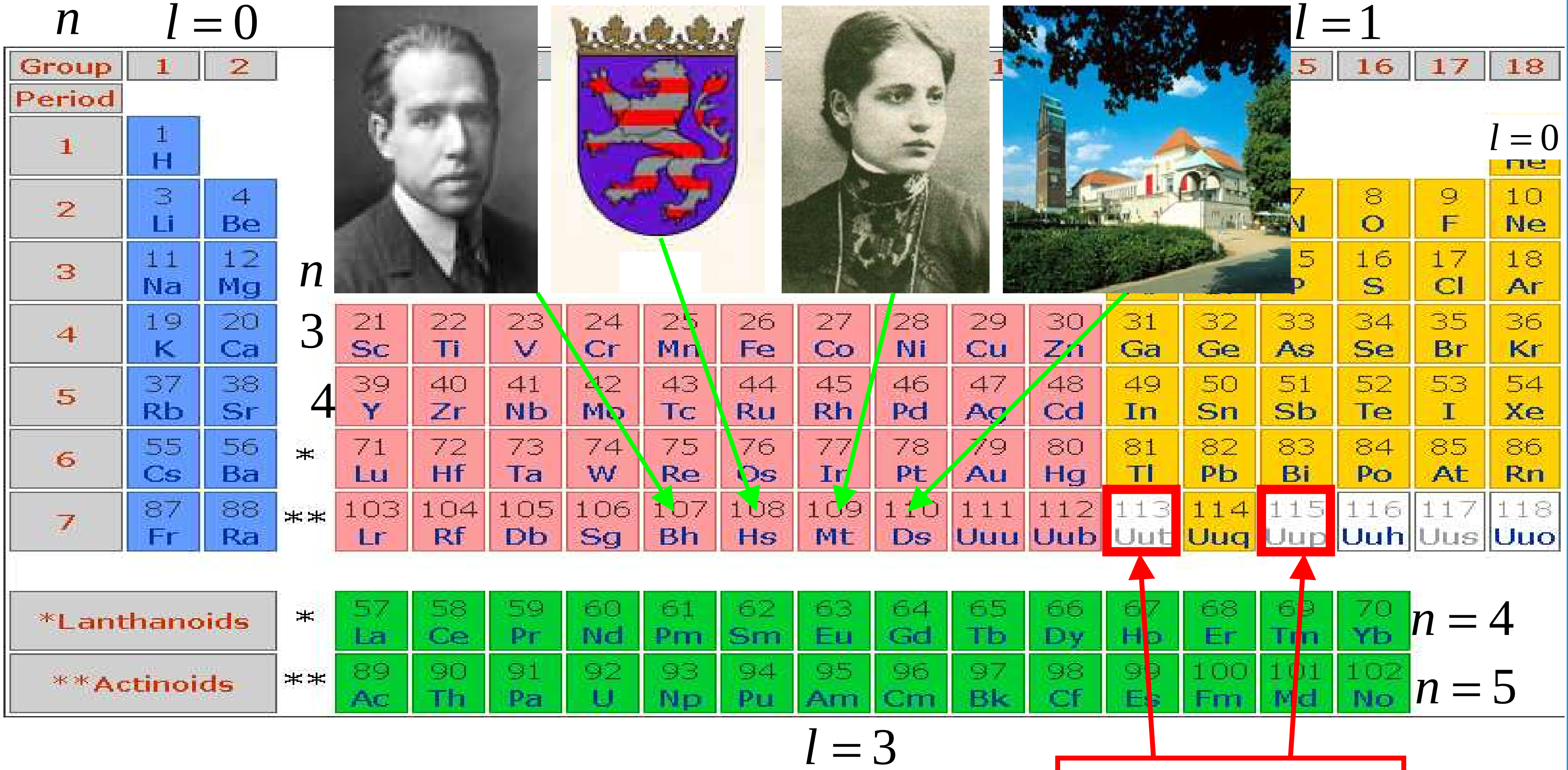
The periodic table

05/06/2005



- Fill pattern of outermost electrons:

  n=1: 2 with l=0

  n=2: 2 with l=0, then 6 with l=1

  n=3: 2 with l=0, then 6 with l=1, but then not 10 with l=2

  Since the n=4, l=0 states have a probability close to the core and their energy is lowered.

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The total angular momentum

$$E = V(r) + \frac{1}{2m}(p_r^2 + \frac{1}{r^2}\vec{L}^2) + A\vec{L}\cdot\vec{S} = \frac{1}{2m}(p_r^2 + \frac{1}{r^2}\vec{L}^2) + \frac{A}{2}[(\vec{L}+\vec{S})^2 - \vec{L}^2 - \vec{S}^2]$$

$$V(r) + \frac{1}{2m}p_r^2 + (\frac{1}{2mr^2} - \frac{A}{2})\vec{L}^2 + \frac{A}{2}[\vec{J}^2 - \vec{S}^2], \quad \vec{J} = \vec{L} + \vec{S}$$

Spin orbit coupling

The Schrödinger equation

$$[V(r) + (\frac{1}{2mr^2} - \frac{A}{2})\hbar^2 l(l+1) - \frac{A}{2}\hbar^2\frac{3}{4}]\Phi + \frac{1}{2m}\hat{p}_r^2\Phi + \frac{A}{2}\hat{\vec{J}}^2\Phi = E\Phi$$

Where again a simultaneous eigenfunction of L^2 was chosen.

One can additionally choose simultaneous eigenfunctions of J^2 since

$$[\hat{\vec{L}}^2, \hat{\vec{J}}^2] = [\hat{\vec{L}}^2, \hat{\vec{L}}^2 + 2L_iS_i + \hat{\vec{S}}^2] = 0$$

The total angular momentum J has angular momentum commutators

$[\hat{J}_i, \hat{J}_j] = i\hbar\varepsilon_{ijk}\hat{J}_k$ and therefore $\hat{\vec{J}}^2$ has eigenvalues $\hbar^2 j(j+1)$

This leads to a one dimensional Schrödinger equation

$$[V(r) + (\frac{1}{2mr^2} - \frac{A}{2})\hbar^2 l(l+1) + \frac{A}{2}\hbar^2\{j(j+1) - \frac{3}{4}\}]\Phi + \frac{1}{2m}\hat{p}_r^2\Phi = E\Phi$$

were the set of eigenfunctions depends on l and j: $\Phi \propto R_{nlj}(r)\,, \quad E = E_{nlj}$

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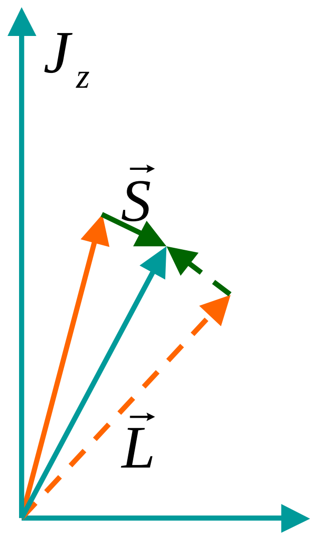
Eigenvalues for J_z?

$$\hat{J}_z \left| n\, l\, j\, s\, m_j \right\rangle = (\hat{L}_z + \hat{S}_z) \sum_{m_l=-l}^{l} \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} \left| n\, l\, m_l\, s\, m_s \right\rangle C_{m_l\, m_s}^{m_j}$$

$$= \hbar \sum_{m_l=-l}^{l} \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} (m_l + m_s) \left| n\, l\, m_l\, s\, m_s \right\rangle C_{m_l\, m_s}^{m_j}$$

$$m_j = m_l \pm \tfrac{1}{2}$$



Note that L_z and S_z cannot be without spread when Jz is fixed.

Largest possible eigenvalue for J_z: $m_j = l + \tfrac{1}{2}$

Other eigenvalues of J_z can be obtained by the lowering operator J_-: $m_j \in \{-l - \tfrac{1}{2}, \ldots, l - \tfrac{1}{2}, l + \tfrac{1}{2}\}$

$$\left| n\, l\, j\, s\, m_j \right\rangle = A \left| n\, l, m_l = m_j - \tfrac{1}{2}, s\, m_s = \tfrac{1}{2} \right\rangle + B \left| n\, l, m_l = m_j + \tfrac{1}{2}, s\, m_s = -\tfrac{1}{2} \right\rangle$$

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Total angular momentum states

$$|\Psi\rangle = \sum_{\text{all } n}\sum_{\text{all } l}\sum_{m_l=-l}^{l}\sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} A_{n l m_l m_s}|n\,l\,m_l\,s\,m_s\rangle = \sum_{\text{all } n}\sum_{\text{all } l}\sum_{\text{all } j}\sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} B_{n l j m_j}|n\,l\,j\,s\,m_j\rangle$$

Where the eigenstates of J^2 are linear combinations of the previously arbitrarily chosen eigenstates of L_z and S_z:

$$|n\,l\,j\,s\,m_j\rangle = \sum_{m_l=-l}^{l}\sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} |n\,l\,m_l\,s\,m_s\rangle\, C_{m_l m_s}^{m_j}$$

$$C_{m_l m_s}^{m_j} = \langle n\,l\,m_l\,s\,m_s | n\,l\,j\,s\,m_j\rangle$$

The basis states are now simultaneous eigenfunctions of:

$$\hat{E}|n\,l\,j\,s\,m_j\rangle = E_{nl}|n\,l\,j\,s\,m_j\rangle$$

$$\hat{\vec{L}}^2|n\,l\,j\,s\,m_j\rangle = \hbar^2 l(l+1)|n\,l\,j\,s\,m_j\rangle$$

$$\hat{\vec{J}}^2|n\,l\,j\,s\,m_j\rangle = \hbar^2 j(j+1)|n\,l\,j\,s\,m_j\rangle$$

$$\hat{\vec{S}}^2|n\,l\,j\,s\,m_s\rangle = \hbar^2 \tfrac{3}{4}|n\,l\,j\,s\,m_s\rangle$$

$$\hat{J}_z|n\,l\,j\,s\,m_j\rangle = \hbar m_j|n\,l\,j\,s\,m_j\rangle$$

Note that having eigenstates of Jz as basis states is an arbitrary choice since all liner combinations

$$\sum_{m_j=-j}^{j}|n\,l\,j\,s\,m_j\rangle A_{m_j}$$

have the same energy.

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Classification of states in Hydrogen

1) Main quantum number:

Number of states with n: $N_n = \sum_{l=0}^{n-1} \sum_{m=-l}^{l} 2 = \sum_{l=0}^{n-1} 2(2l+1) = 4\frac{(n-1)n}{2} + 2n = 2n^2$

$$3^2\mathrm{p}_{3/2}$$

2) Orbital angular momentum quantum number:

Notation for l = 0 1 2 3 4 5 …

s p d f g h …

3) Total angular momentum quantum number:

As trailing subscript: j = 1/2 3/2 5/2 …

4) Multiplicity of the fine structure:

As leading superscript: 2 for one electron and its 2 spin states.

Systems with more than one electron:

Orbital angular momentum of the full atom:

Notation for l = 0 1 2 3 4 5 …

S P D F G H …

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Fine structure of Hydrogen

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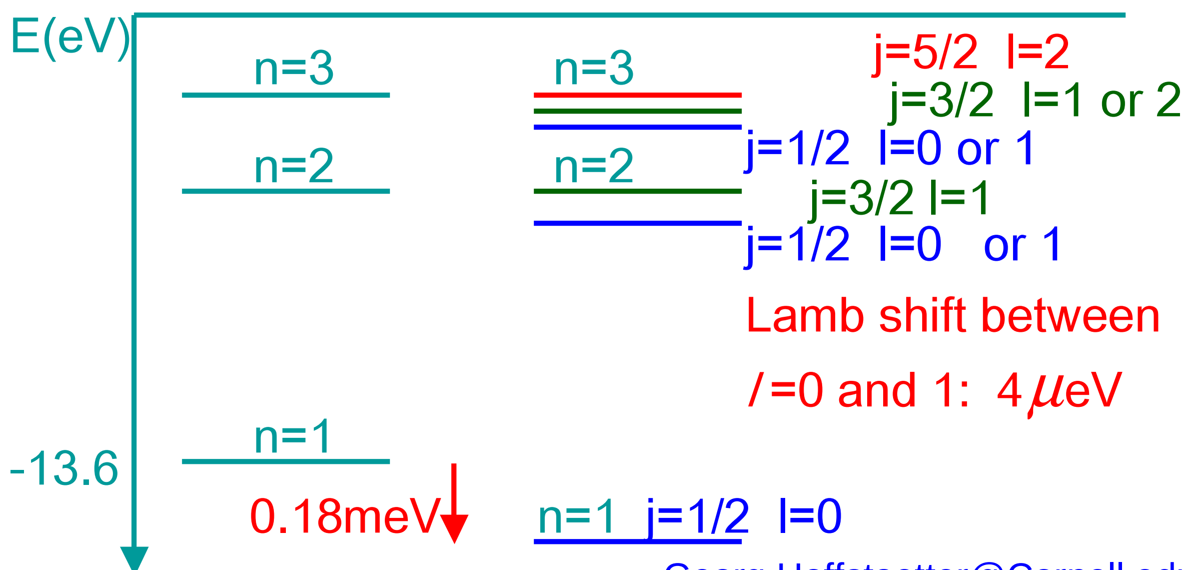
A full relativistic treatment, including spin-orbit coupling leads to

$$E_{nl\,j} = E_n[1+\frac{\alpha^2}{n}(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n})]$$

- No dependence on *l*: This is a special feature of the Coulomb 1/r potential. It disappears when the 1/r potential is changed for example by electrons in inner shells.
- There cannot be a dependence on m_j , due to rotational symmetry. Classical picture: Changing m_j for fixed j does not change the angle between J and S.

Willis Eugene Lamb
born 1913



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