

Multi-electron atoms: L-S coupling, j-j coupling

- The optical spectrum and chemical properties are determined by electrons not in shells -- the valence electrons.
- For multi-electron atoms we split the Hamiltonian as follows:

$$H = H_{CF} + H'$$

↑ central field.

$$H_{CF} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{CF}(r_i) \right]$$

$$H' = \sum_{i=1}^N \left\{ \sum_{j>i}^N \frac{e^2}{r_{ij}} - S(r_i) \right\}$$

where

$$V_{CF}(r) = -\frac{Ze^2}{r} + S(r)$$

$V_{CF}(r)$ is determined via Hartree-Fock method.

$$\Psi \text{ (spin-orbital)} \leftarrow H_{CF}$$

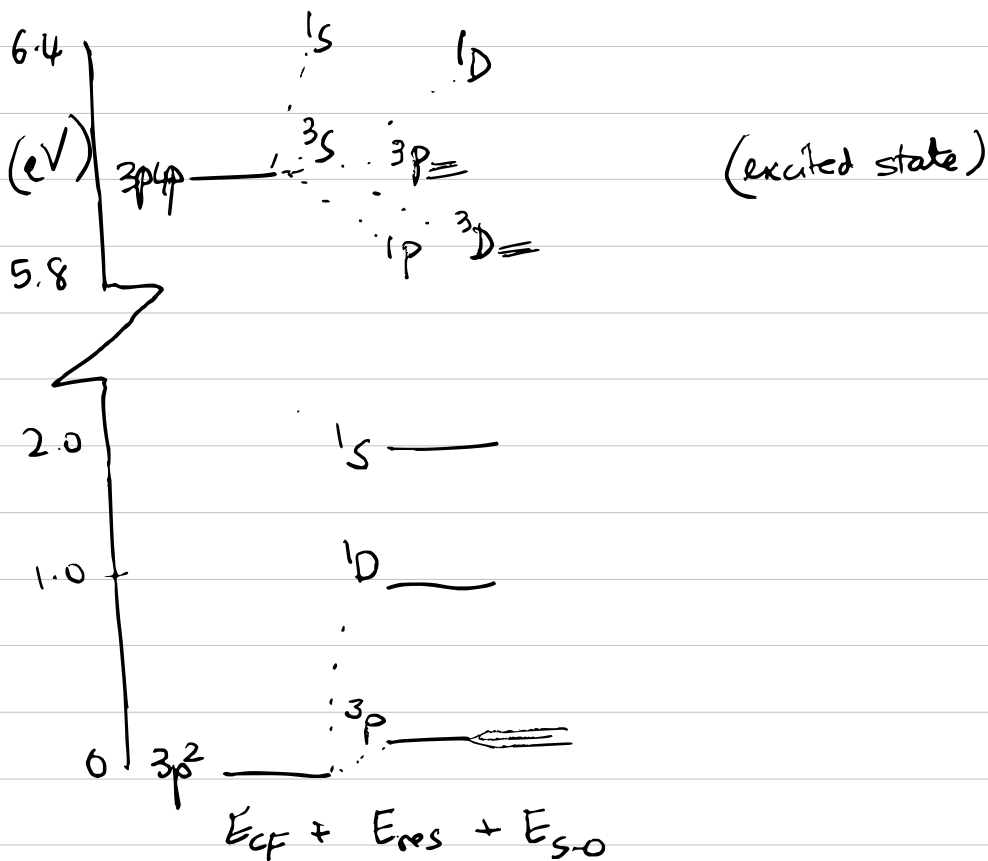
The remaining portion of the Hamiltonian is residual electrostatic interaction. In addition we have

spin-orbit interaction

relativistic correction

which are not included in H'

Silicon



○ Consider two valence electrons, p^2 . For the spin-part we have

$\Psi_{\text{spin}}^A \dots$ anti-symmetric (singlet)

$\Psi_{\text{spin}}^S \dots$ symmetric (triplet)

[The spin-magnetic-spin-magnet interaction is weak]
How about the spatial wave-function?

○ The total angular momentum $\vec{J} = \vec{L} + \vec{S}$ is a constant (in absence of any external torque)

● We ignore spin-orbit interaction and relativistic correction. The $\vec{L} = \vec{l}_1 + \vec{l}_2$ is constant (even though \vec{l}_1 and \vec{l}_2 precess due to electrostatic interaction)

● We have accounted for \vec{S}_1 and \vec{S}_2 by

$\Psi_{\text{spin}}^A, \Psi_{\text{spin}}^S$.

So $\vec{S} = \vec{S}_1 + \vec{S}_2$ is also constant

$$\text{Thus } [L^2, H'] = 0, \quad [L_z, H'] = 0$$

$$[S^2, H'] = 0, \quad [S_z, H'] = 0$$

$$\text{Thus instead of } |l, m, s, m_s\rangle \\ |l_1, m_1, s_1, m_{s1}\rangle \\ |l_2, m_2, s_2, m_{s2}\rangle$$

Our spatial wave-function is

$$\Psi = \Psi(n_1, l_1, m_1) \times \Psi(n_2, l_2, m_2)$$

From the discussion above it is clear that this product can be decomposed to spherical harmonics

$$\Psi = \sum_k \alpha_k \Psi(L_k, M_k)$$

↑ Clebsch-Gordan coeff

$$k = |l_1 - l_2| \text{ to } |l_1 + l_2|$$

A simple example of Clebsch-Gordan coefficients
is $s_1 = \frac{1}{2}$ $s_2 = \frac{1}{2}$

$$S = 0, 1$$

$$|S=0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

$$|S=1\rangle = \begin{array}{c} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{array}$$

$$\frac{1}{\sqrt{2}} (|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle)$$

thus, if \vec{L} and \vec{S} remain constant we
are back to hydrogen solutions but
with L and S .

Fine-structure:

We have two additional terms

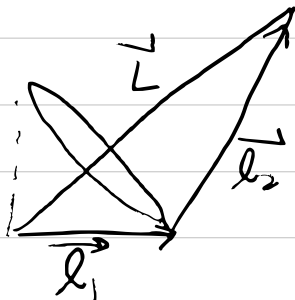
- spin-orbit interaction
- special relativity

↑ ignored, especially for
high Z atoms, large n

recall, $v = \frac{\alpha c}{n}$

spin-orbit

$$H_{s-o} = \beta_1 \vec{l}_1 \cdot \vec{s}_1 + \beta_2 \vec{l}_2 \cdot \vec{s}_2$$



Note \vec{l}_1, \vec{l}_2 precess (due to electrostatic interaction) but \vec{L} is constant.

Classically $\vec{l}_1 \cdot \vec{L}$ is constant

$$\therefore l_1 \rightarrow \frac{\vec{l}_1 \cdot \vec{L}}{|\vec{L}|^2} \vec{L} \rightarrow \frac{\langle \vec{l}_1 \cdot \vec{L} \rangle}{L(L+1)} \vec{L}$$

$$\text{Thus } H_{s-o} = \beta_1 \frac{\langle \vec{s}_1 \cdot \vec{s} \rangle}{s(s+1)} \vec{s} \cdot \frac{\langle \vec{l}_1 \cdot \vec{L} \rangle}{L(L+1)} \vec{L} +$$

$$\beta_2 \frac{\langle \vec{s}_2 \cdot \vec{s} \rangle}{s(s+1)} \vec{s} \cdot \frac{\langle \vec{l}_2 \cdot \vec{L} \rangle}{L(L+1)}$$

$$= \beta_{so} \langle \vec{L} \cdot \vec{s} \rangle$$

$$E_{s-o} = \beta_{Ls} \langle \vec{L} \cdot \vec{S} \rangle$$

$$= \frac{\beta_{Ls}}{2} \{ J(J+1) - L(L+1) - S(S+1) \}$$

⇒ Lande "interval rule"

$$E_{s-o}(J) - E_{s-o}(J-1) = \beta_{Ls} J$$

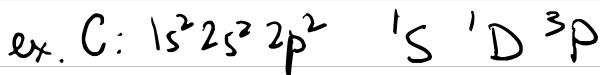
Hund's Rules: Ground state electron config.

For < half-filled shells

- Highest S is lowest in energy
- Highest L is lowest in energy
- Lowest J is lowest in energy.

For > half-filled shells

- Highest J is lowest in energy



1S —

1D —

3P — $\left\{ \begin{array}{l} \leftarrow J=2 \\ \leftarrow J=1 \\ \leftarrow J=0 \end{array} \right.$

SELECTION RULES (E1: Electric Dipole)

rigorous	[$\Delta J = 0, \pm 1$ (but not $0 \rightarrow 0$)	Level
		Parity changes	Configuration
		$\Delta l = \pm 1$ one-electron jump	Configuration
$L \neq S$	[$\Delta L = 0, \pm 1$ (but not $0 \leftrightarrow 0$)	Term
coupling		$\Delta S = 0$	Term

SELECTION RULES (M1: magnetic dipole)

$$\Delta J = 0, \pm 1 \quad (\text{but not } 0 \leftrightarrow 0)$$

No parity change

$$\Delta l = 0$$

$$\Delta n = 0$$

$$\Delta L = 0$$

$$\Delta S = 0$$

- Even weaker transitions include E2, E3, M2 !

j-j coupling :

In figure (next page)

- Gross-structure: energy to excite an electron from ground state to first excited state
- Residual electrostatic energy:
singlet-triplet separation of lowest excited electronic configuration
- x Fine-structure: splitting of lower P levels

Next, recall for alkali atoms, the spin-orbit energy is

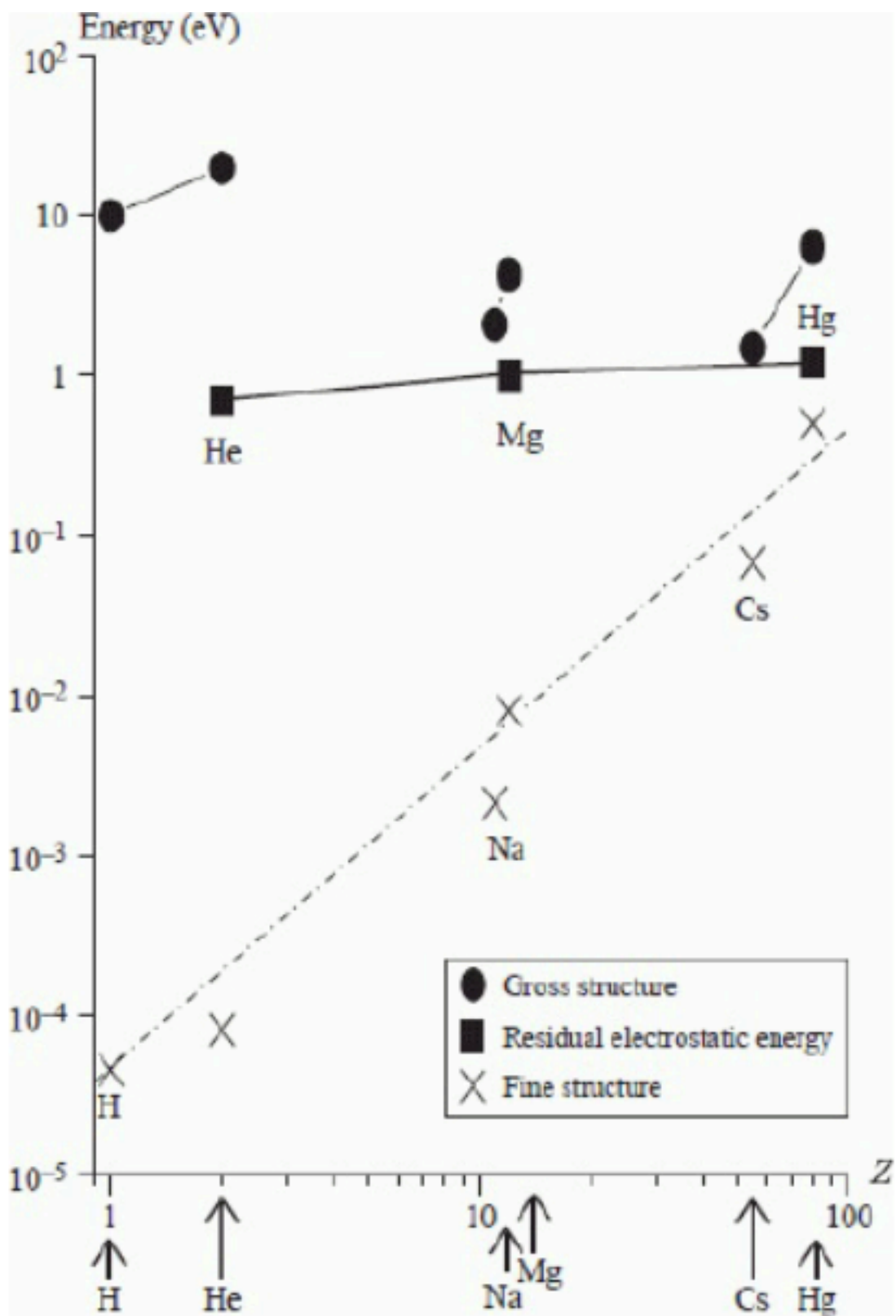
$$E_{so} = \beta \{ j(j+1) - l(l+1) - s(s+1) \}$$

$$\beta = \frac{Z_i^2 Z_o^2}{n^{*3} l(l+1)} \alpha^2 hc R_{\infty}$$

n^* ... effective principal quantum number

Z_i ... inner atomic number $\rightarrow Z$

Z_o ... outer atomic number $\rightarrow 1$



When

residual electrostatic \gg spin-orbit

\Rightarrow L-S coupling

residual electrostatic \ll spin-orbit

\Rightarrow j-j coupling

