

Before considering the effect of a magnetic field we note that, if $V_{ee}(r_i)$ is estimated properly, the residual contribution to the electron-electron repulsion

$$\mathcal{H}^1 = \frac{1}{2} \sum_{i \neq j} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{|r_i - r_j|} - \sum_i V_{ee}(r_i) \quad (1.60)$$

shall be small and, as such, can be treated as a perturbation.

What can we say about the strength of the Zeeman and spin-orbit interaction in comparison with the $\mathcal{H}_{0,i}$ Hamiltonian? The spacing between atomic levels defined by the $\mathcal{H}_{0,i}$ Hamiltonian falls typically in the range 1 – 10 eV, while for applied fields in the range 1 – 10 T (in ordinary laboratories magnetic fields hardly exceed this upper bound) the interaction \mathcal{H}_Z is of the order of 0.1 – 1 meV \simeq 1 – 10 K. Thus, the Zeeman interaction can be safely treated as a perturbation with respect to $\mathcal{H}_{0,i}$. We will see later that the Zeeman splitting is actually comparable with the thermal energy $k_B T$ and this is one of the reasons why statistical physics will be needed. The Zeeman interaction is associated with the *paramagnetic* response of an atom.

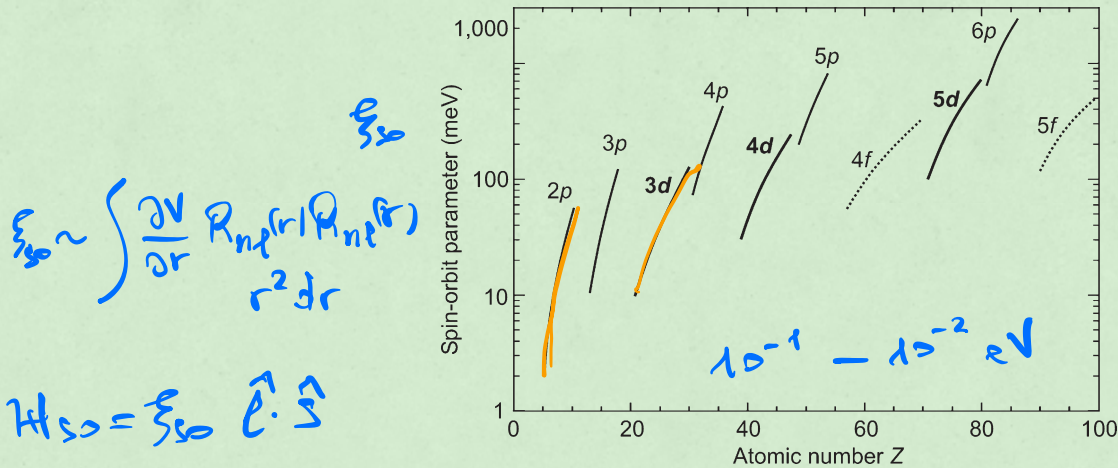
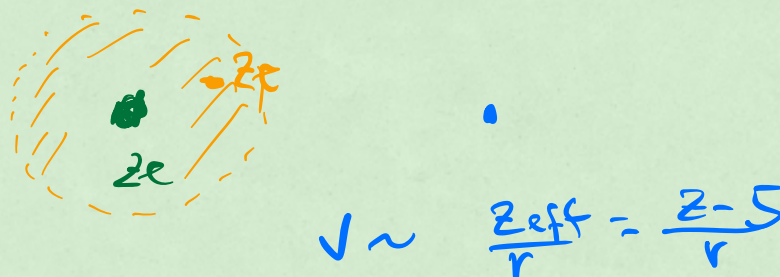
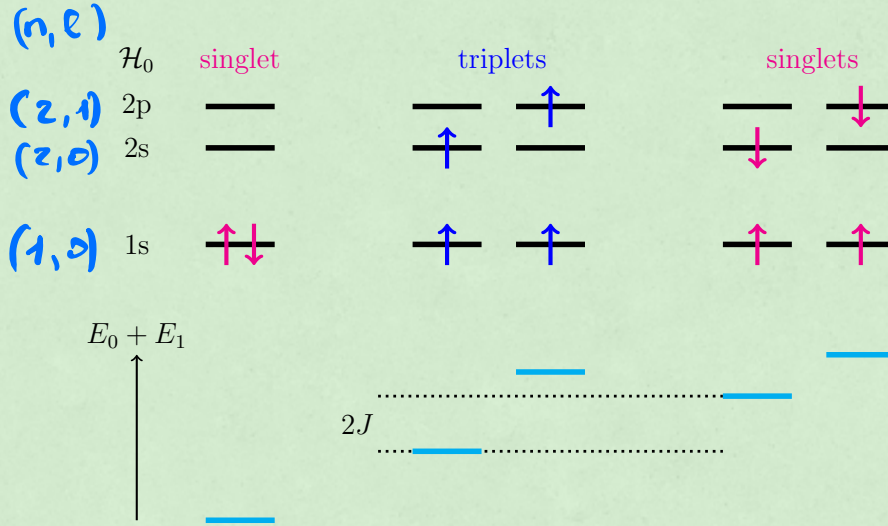


Figure 1.1: Theoretical values for the spin-orbit parameter ζ_{nl} , defined in Eq. (1.61), obtained by the relativistic Hartree-plus-statistical-exchange method for the valence shell of the neutral atoms in their ground state. Taken from R. D. Cowan, *The theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981). Reproduced in Chapter 6 of “*Magnetism: from Fundamentals to Nanoscale Dynamics*”, by J. Stöhr and H. C. Siegmann (2006) available in the [BookChapters](#) folder.

For what concerns the spin-orbit interaction, the operator ξ_{so} defined in





The picture depicted above is consistent with a series of transitions that only occur within a given spin subspace – the singlet or the triplet. In fact, in the electric-dipole approximation, transitions between levels associated with different spin states are forbidden (only transitions involving $\Delta S = 0$ and $\Delta L = \pm 1$ are allowed to the first order). This scenario was actually puzzling in the early decades of the last century. The seminal works of Heisenberg to interpret the emission spectrum of neutral He thus pinpointed the importance of spin in defining the scheme of the energy levels in atoms and the allowed/forbidden transitions among them. Starting from those works Heisenberg developed the concept of exchange interaction in the late 1920s. Particular influential was his proposal to express the splitting between singlet and triplet state for the occupation of the same single-electron levels, e.g. (1s)(2s) or (1s)(2p), in terms of an effective coupling between spins. Using the fact that $(\hat{\mathbf{S}})^2 = (\hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2)^2 = (\hat{\mathbf{s}}_1)^2 + 2\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2 + (\hat{\mathbf{s}}_2)^2$, we have seen in one of the **Assignments** that the *effective* spin Hamiltonian

$$\mathcal{H}_{\text{exch}} = -2J \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2 \quad (1.71)$$

has eigenvalues

$$\begin{aligned} \langle \chi_{0,0} | \mathcal{H}_{\text{exch}} | \chi_{0,0} \rangle &= +\frac{3}{2}J && \text{for the singlet} \\ \langle \chi_{1,m} | \mathcal{H}_{\text{exch}} | \chi_{1,m} \rangle &= -\frac{1}{2}J && \text{for the triplet,} \end{aligned} \quad (1.72)$$

meaning that this operator exactly reproduces the splitting existing between the singlet and the triplet state of a given electronic configuration. Note

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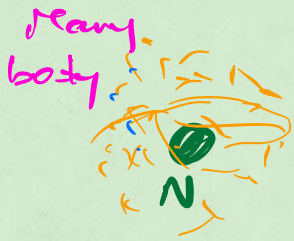
Dirac \Rightarrow 1) $e^- \uparrow \quad S = 1/2$

2) $H_Z = \mu_B (\hat{l} + 2\hat{S}) \cdot \vec{B}$ $\uparrow \vec{B}$

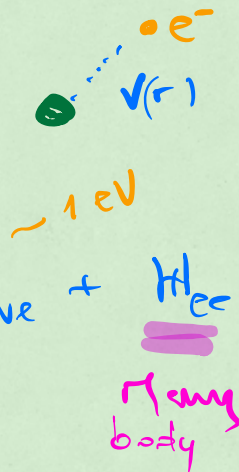
3) $H_{so} = \xi_{so} \hat{l} \cdot \hat{S}$

4) $\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \Rightarrow \psi = \varphi(r) | \sigma \rangle \quad (\sigma = \pm 1/2)$
 \longleftarrow Spatial/orbital dof
 \longleftarrow Spin dof

to look at atom : free ion



\Rightarrow



single part. Pb
 $H_{ee} \approx H_{ee}^0 + H_{ee}^1$
Pert.

$H = H_{kin} + H_{Ne} + H_{ee}$

$H = H_{kin} + H_{Ne} + H_{ee}^0 + H_{ee}^1$
 $\underbrace{\hspace{10em}}$
 H_0

z electrons

$H_0 = \sum_i H_{0,i}$ S.P.

Schrödinger eq.

Central Potential.

$$H_{0,i} \Psi_{nlm}(\mathbf{r}_i) = H_{0,i} \underbrace{R_{nl}(r_i)}_{\text{radial}} \underbrace{Y_{lm}(\phi_i, \theta_i)}_{\text{angular}}$$

$$H_{0,i} \Psi_{nlm}(\mathbf{r}_i) = E_{nl} \Psi_{nlm}(\mathbf{r}_i)$$

SPATIAL D.O.F. $\sim \sim$

- (n, l, m) single electron levels \Rightarrow Periodic Table
- ξ_{so} is determined by solution 3.P. with the central potential including screening effect of other e^-

Role of SPIN D.O.F.
 Symm A. symm
 $\Psi^S(\mathbf{r}_1, \mathbf{r}_2) | \text{Spin} \rangle$
 singlet

2 or more e^-
 A. Symm. Symm
 $\Psi^T(\mathbf{r}_1, \mathbf{r}_2) | \text{Spin} \rangle$
 triplet

$$\Psi^S(\mathbf{r}_1, \mathbf{r}_2) = \Psi^S(\mathbf{r}_2, \mathbf{r}_1)$$

$$\Psi^T(\mathbf{r}_1, \mathbf{r}_2) = -\Psi^T(\mathbf{r}_2, \mathbf{r}_1)$$

$\hat{S}_1 \cdot \hat{S}_2$

$$|G_1 \sigma_2\rangle = |++\rangle | - + \rangle | + - \rangle | -- \rangle$$

	$\chi_{1,1}$ ++	-+	+ -	$\chi_{1,-1}$ --
++	1/4			0
-+		-1/4	1/2	
+ -		1/2	-1/4	
--	0			1/4

$$\hat{S}_1 \cdot \hat{S}_2 = \hat{S}_1^x \hat{S}_2^x + \hat{S}_1^y \hat{S}_2^y + \hat{S}_1^z \hat{S}_2^z$$

1) diag $\hat{S}_1^z \hat{S}_2^z |++\rangle = \frac{1}{4} |++\rangle$
 $| - + \rangle = -\frac{1}{4} | - + \rangle$

2) $\hat{S}_1^x \hat{S}_2^x |++\rangle = \frac{1}{4} | -- \rangle$ $\left| \begin{array}{l} \hat{S}_1^y \hat{S}_2^y |++\rangle = -\frac{1}{4} | -- \rangle \\ \hat{S}_1^y \hat{S}_2^y | - + \rangle = +\frac{1}{4} | + - \rangle \end{array} \right.$

MATRIX

$$\frac{1}{4} \begin{pmatrix} -1 & 2 \\ 2 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \Rightarrow \frac{|+-\rangle + |-+\rangle}{\sqrt{2}} \quad \chi_{1,0}$$

$$\frac{1}{4} \begin{pmatrix} -1 & 2 \\ 2 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{-1}{4} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \Rightarrow \frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \quad \chi_{0,0}$$

$$\hat{S}_1 \cdot \hat{S}_2 = \frac{1}{2} (\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \neq$$

$$\hat{S}_1 \hat{S}_2 |S, m\rangle = E(S) |S, m\rangle$$

$$S = |s_1 - s_2| \dots s_1 + s_2$$

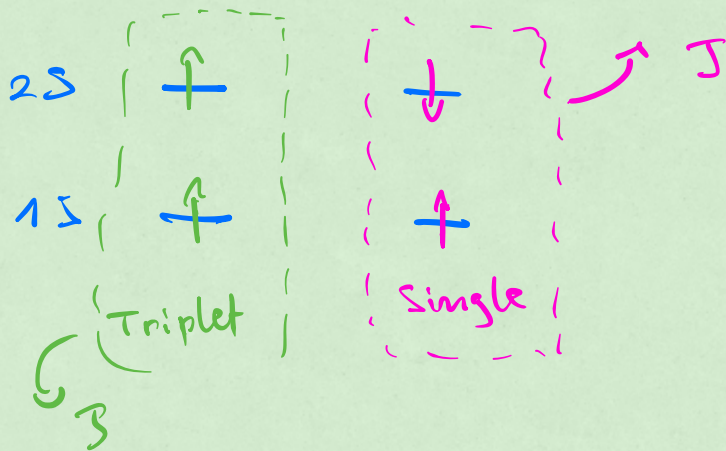
$$S = 0, 1$$

$$E(S) = \frac{1}{2} [S(S+1) - \underbrace{s_1(s_1+1)}_{3/4} - \underbrace{s_2(s_2+1)}_{3/4}]$$

$$E(S) = \frac{1}{2} S(S+1) - \frac{3}{4}$$

$S=1 \rightarrow \frac{1}{4}$
 $S=0 \rightarrow -\frac{3}{4}$

$$H_{\text{exch}} = -2J \hat{S}_1 \cdot \hat{S}_2 \left[\begin{array}{l} S=0 \quad 3/2 J \\ S=1 \quad -1/2 J \end{array} \right] 2J$$



Weyl
Theorem more than 2 electrons.

States belonging to the same multiplet of total S have the same symmetry w.r.t. to the exchange of any pair of (i, j) electrons

Ex. 4 electrons $(\sigma_1 \sigma_2 \sigma_3 \sigma_4)$

$| - + - - \rangle$
 $(+ + - -)$

$$2^4 = 1$$

$$S = (2, 1, 0)$$

$\rightarrow | + + + + \rangle \rightarrow M_S = 2$

$\rightarrow | - - - - \rangle \rightarrow M_S = -2$

$(+ + +) \quad M_S = +3/2 \quad S = \underline{3/2}, 1/2$

$+1/2$
 $-1/2$

25H states $\Rightarrow 4$

$S^+ | - - - \rangle \quad M_S = -3/2$