

## Lecture 14: Correlation effects: L-S and j-j coupling

Let us recall the fundamental Hamiltonian for multielectron atoms includes

$$H_0 = \sum_i \left( \frac{p_i^2}{2} - \frac{Z}{r_i} \right) \quad \text{Each electron's attraction to the nucleus}$$

$$H_1 = \sum_{i < j} \frac{1}{r_{ij}} \quad \text{Electron-electron repulsion}$$

$$H_2 = \sum_i \xi(r_i) \vec{l}_i \cdot \vec{s}_i \quad \text{Spin-orbit coupling}$$

$H_3 =$  Other relativistic corrections including kinetic energy, electron spin-spin interaction, nuclear effects (hyperfine) etc.

Because of the strong electron-electron interaction and identical particle requirements, it is not possible to solve this in standard perturbation theory. We have only two fundamental symmetries

(1) Rotation

(a) Inversion  $\Rightarrow$  Parity is a good q-number

If we ignore hyperfine interaction

$$(1) \Rightarrow \vec{J} = \sum_i (\vec{l}_i + \vec{s}_i) = \sum_i \vec{j}_i = \vec{L} + \vec{S}$$

$J, M_J$  are good q-number

Define  $J, M, \Pi$  is not sufficient to break up the problem into tractable subspaces.

The approach then is to use mean-field theory to make a central field approximation so that

$$H_0 + H_1 \Rightarrow H_0' + H_1'$$

$$\text{where } H_0' = \sum_i \left( \frac{p_i^2}{2m} - \frac{Z}{r_i} + S(r_i) \right)$$

$$H_1' = \sum_{i < j} \frac{1}{r_{ij}} - S(r_i)$$

$$S(r_i) = \left\langle \frac{1}{r_{ij}} \right\rangle_j \quad \text{screening potential}$$

The effective central potential  $V_{\text{central}} = \frac{-Z}{r_i} + S(r_i)$

is determined self-consistently through the

Hartree-Fock approximation, whereby by we

take as our ansatz for the multielectron wavefunction a single Slater determinant.

$$\Psi(0, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_\alpha(1) & \phi_\beta(1) & \dots & \phi_\nu(1) \\ \phi_\alpha(2) & \phi_\beta(2) & \dots & \phi_\nu(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_\alpha(N) & \phi_\beta(N) & \dots & \phi_\nu(N) \end{vmatrix}$$

With  $\phi_\alpha(i) = \underbrace{R_{n_\alpha l_\alpha}(r_i)}_{\text{radial}} \underbrace{Y_{l_\alpha m_\alpha}(\theta_i, \phi_i)}_{\text{angular}}$   $|m_\alpha\rangle_i$   
 Central potential orbitals  $u_\alpha(\vec{r}_i)$

Which under a variational calculation satisfy

$$H_0 u_\alpha(\vec{r}) + \left( \sum_{\beta} \int d\vec{r}' \frac{|\psi_{\beta}(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} \right) u_\alpha(\vec{r}) - \left( \sum_{\beta} \delta_{m_\alpha m_\beta} \int d\vec{r}' \frac{u_{\beta}^*(\vec{r}') u_{\alpha}(\vec{r}')}{|\vec{r} - \vec{r}'|} \right) u_{\beta}(\vec{r}) = E_{\alpha} u_{\alpha}(\vec{r})$$

These are typically solved for self-consistently by starting with some set  $\{u_{\alpha}(\vec{r})\}$ , defining the direct and exchange terms and iterating.

As set of orbital  $\{ (n_\alpha, l_\alpha) (n_\beta, l_\beta) \}^{k_e}$  define an electron configuration.

One correction to Hartree Fock, within the central field approximation is the Configuration Interaction, whereby we take as our ansatz a superposition of Slater Determinants.

The next two dominant effects are  $H_1'$  (residual Coulomb interaction from non-spherical symmetric seen by each electron) and  $H_2$  (spin-orbit). There are two cases that come up  $H_1' \gg H_2$  (Russell-Saunders or L-S case) vs  $H_2 \ll H_1'$  ( $j-j$  case). Recall that spin-orbit energy scales as  $Z^4$ . Thus, for very highly charged nuclei  $H_2$  can dominate if there are few other electrons around. Typically though  $H_1'$  dominates  $H_2$  especially for the lighter elements.

• Russell-Saunders L-S coupling

$$H^r = \sum_{i < j} \left( \frac{1}{r_{ij}} - \left\langle \frac{1}{r_{ij}} \right\rangle_{\text{config}} \right)$$

We treat this as a perturbation within a degenerate configuration. The screening potential is thus an overall constant, and does not affect the splitting.

Note:  $H^r$  is invariant separately by rotations in space of all electron

⇒ Rotation generated by total orbital ang mom

$$\vec{L} = \sum_{i=1}^N \vec{l}_i$$

Also commutes with total spin  $\vec{S} = \sum_{i=1}^N \vec{s}_i$

## Terms from a given configuration

A configuration is defined by a set of occupied subshells

$$(n_a l_a)^{k_a} (n_b l_b)^{k_b} \dots$$

Electrons in the same subshell are said to be "equivalent" and in different subshells "non-equivalent". We seek the possible values of  $L$  and  $S$  that can arise for a given configuration. One can use the rules of addition of angular momentum (the triangle rule) to get possible  $q$ -numbers. However not all values are consistent with the antisymmetrization constraint for equivalent electrons. For example, the  $(1s)^2$  ground-state configuration of He. By addition of angular momentum  $L=0$ ,  $S=0,1$ . However  $L=0$  is symmetric spatially  $\Rightarrow$  can only have anti-symmetric spin  $\Rightarrow S=0 \Rightarrow$  Term  $^1S_{\text{sym}}$   $L=0$  no  $^3S$

Let us consider config. with non-equivalent electrons

$$Eg \quad (n p)(n' p) \Rightarrow l_n = l_p = 1 \quad s_n = s_p = \frac{1}{2}$$

$$\Rightarrow \text{Can have } L=0, 1, 2, \quad S=0, 1$$

$$6 \text{ possible terms: } \begin{cases} ^1S & ^1P & ^1D \\ ^3S & ^3P & ^3D \end{cases}$$

Now consider a third orbital  $n^2 p n^2 d$   
 We add the the  $n^2 d$  to each term

$$\begin{aligned}
 (L=2, S=\frac{1}{2}) &\rightarrow {}^2S \quad (L=0, S=0) \Rightarrow (L=2, S=\frac{1}{2}) \quad {}^2D \\
 &\rightarrow {}^2P \quad (L=1, S=0) \rightarrow (L=1, 2, 3, S=\frac{1}{2}) \quad {}^2S, {}^2P, {}^2D, {}^2F, {}^2G \\
 &{}^3S \quad (L=0, S=1) \rightarrow (L=2, S=\frac{1}{2}, \frac{3}{2}) \quad {}^3D, {}^3D \\
 &\text{etc.}
 \end{aligned}$$

For equivalent electrons:

Closed shell  $(nl)^{2(2l+1)}$  all possible  $M_L$  and  $M_S$   
 $\Rightarrow$  only  $M_L=0, M_S=0$

$\Rightarrow$  Only one possible term  ${}^1S$

Closed shells are singlet  $-S$  always.

The rest is determined by the valence shell

Consider Carbon with valence shell  $(2p)^2$

By addition of ang. momentum  $L=0, 1, 2$   
 (ignoring identical particles)  $S=0, 1$

We would have degeneracy of 36 sublevels.

However for  $(nl)^k$ , degeneracy =  $\binom{2l+1}{k}$

Here  $\frac{6!}{2! \cdot 4!} = 15 \Rightarrow$  Fewer allowed

To determine the possible terms that can arise from configurations of equivalent electrons in the same shell, we enumerate all the possible spin orbitals (i.e.  $m_l$  and  $m_s$  values) consistent with the Pauli principle.

Consider the Ground state of Carbon, configuration  $(3p)^2$   
 Below is a table of possible <sup>15</sup> fillings.

	$m_{l1}$	$m_{s1}$	$m_{l2}$	$m_{s2}$	$M_L$	$M_S$
1)	1	$\frac{1}{2}$	1	$-\frac{1}{2}$	2	0
2)	1	$\frac{1}{2}$	0	$\frac{1}{2}$	1	1
3)	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	1	0
4)	1	$\frac{1}{2}$	-1	$\frac{1}{2}$	0	1
5)	1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	0	0
6)	1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	0
7)	1	$-\frac{1}{2}$	0	$-\frac{1}{2}$	1	-1
8)	1	$-\frac{1}{2}$	-1	$\frac{1}{2}$	0	0
9)	1	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1
10)	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0
11)	0	$\frac{1}{2}$	-1	$\frac{1}{2}$	-1	1
12)	0	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	0
13)	0	$-\frac{1}{2}$	0	$\frac{1}{2}$	0	0
14)	0	$-\frac{1}{2}$	-1	$\frac{1}{2}$	-1	-1
15)	-1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0

Now we group the orbitals into number of terms with same  $M_L$  and  $M_S$ . There will always be equal numbers with positive  $M_L$  and negative  $M_L$ . So we keep track only of the positive. We then assign some number of these configurations to terms, as shown in the example below:

$M_S \backslash M_L$	2	1	0
1		1	1
0	1	2	3

↓  $^1D$

$M_S \backslash M_L$	2	1	0
1		1	1
0		1	2

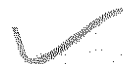
↓  $^3P$

$M_S \backslash M_L$	2	1	0
1			
0			1

↓  $^1S$

⇒ Three terms

$$\begin{aligned}
 ^1D & (2 \cdot 2 + 1) = 5 \text{ sublevel} \\
 ^3P & (2 \cdot 1 + 1)(2 \cdot 1 + 1) = 9 \text{ sublevel} \\
 ^1S & 1 \cdot 1 = 1 \text{ sublevel} \\
 & \underline{\quad\quad\quad} \\
 & 15 \text{ sublevel}
 \end{aligned}$$





## Half-filled vs. Half-empty subshells

We showed that a completely filled subshell  $(nl)^{2(2l+1)}$  corresponds to a spherically symmetric term  $^1S_0$ .

A configuration with  $k$  fewer electrons,  $(nl)^{2(2l+1)-k}$  those act like  $k$  "positive holes" in the shell.

The resulting hole-repulsion is the same as the electron-repulsion but of opposite sign.

Thus, the possible terms arising from the configurations  $(nl)^k$  and  $(nl)^{2(2l+1)-k}$  are the same.

Example  $(np)^k$

Config	Terms
$(np)^5$	$^2P$
$(np)^4$	$^1S, ^3P, ^1D$
$(np)^3$	$^4S, ^2P, ^2D$ (need a Slater table to prove this)
$(np)^6$	$^1S$

## Equivalent and Non-equivalent electrons

If a configuration contains both equivalent and nonequivalent electrons, we first determine the terms for the equivalent case and then add in the non-equivalent electrons.

## Hund rules:

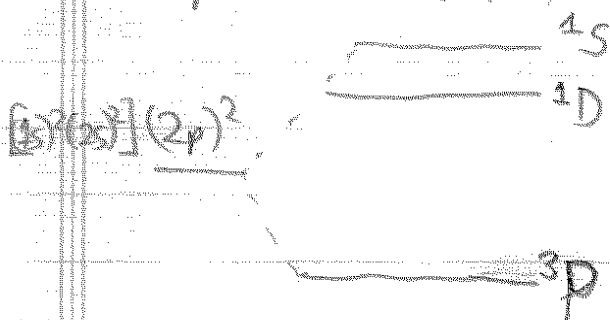
How are the different terms ordered in energy?

There are a set of "empirical" rules that work in Russell-Saunders, and have some physical interpretation

(1) The term with the largest possible value of  $S$  for a given configuration has the lowest energy

(2) For a given  $S$ , the term with the maximum  $L$  has the lowest energy

Example: Carbon



- Hund's rule #1 follows from our earlier discussion; the higher spin states are more spin-symmetric so the spatial wavefunction is more ~~spin~~ anti-symmetric  $\Rightarrow$  Exchange terms are negative and electrons have less repulsion

- Hund's rule #2 is a bit confusing. For single particle orbitals, the electrons with lower orbital ~~penetration~~  $\rightarrow$  the nucleus, and are more tightly bound. For multiple electrons the total angular momentum is determined by the sums of the projections.

States with low angular have many states with electrons orbits in the same direction.

Loosely speaking, the electrons ~~the~~ can "stay further apart" in this case. The opposite is true for low total orbital  $\rightarrow$  opposite  $M_L$ 's  $\Rightarrow$  orbit in opposite directions and pass close



Semi-classical intuition

### Fine-structure: Spin-Orbit

The electrostatic interaction breaks the configuration up into separate terms, each characterized by a given  $L$  and  $S$ , but leaves these terms degenerate with regard to  $J$ . This degeneracy is broken in the  $L$ - $S$  coupling by the spin-orbit perturbation

$$H_2 = \sum_i \xi(r_i) \vec{L}_i \cdot \vec{S}_i, \quad \xi(r_i) = \frac{1}{2m^2c^2} \frac{1}{r_i} \frac{dV(r_i)}{dr_i}$$

To diagonalize we recall that with  $H_2$  the good quantum numbers are  $J, M_J, \Pi, \text{parity}$ .

The parity is fixed by the configuration

$$\Pi = \prod_{i=1}^N (-1)^{l_i}$$

product

For a given term in L-S coupling, we can make states with total  $J, M_J$  in the usual "coupled representation" within a term

$$|k; JM_J; LS\rangle = \sum_{M_L, M_S} \langle JM_J | LM_L SM_S \rangle |k; LM_L SM_S\rangle$$

The energy shift:

$$E_{JM_S}^{(1)} = \langle k; JM_J; LS | H_2 | k; JM_J; LS \rangle$$

$$= \sum_{\substack{M_L, M_S \\ M_L', M_S'}} \sum_l \xi(l) \langle LM_L | \vec{r}_l | LM_L' \rangle \cdot \langle SM_S | \vec{s}_l | SM_S' \rangle \\ \langle JM_J | LM_L SM_S \rangle \langle JM_J | LM_L' SM_S' \rangle$$

By the Landé Projection theorem

$$\langle LM_L | \vec{r}_l | LM_L' \rangle = \frac{\langle L || \vec{r}_l || L \rangle}{L(L+1)} \langle LM_L | L' | LM_L' \rangle$$

$$\langle SM_S | \vec{s}_l | SM_S' \rangle = \frac{\langle S || \vec{s}_l || S \rangle}{S(S+1)} \langle SM_S | S' | SM_S' \rangle$$

$$\therefore E_{JM_S}^{(1)} = \tilde{A} \langle k; JM_J; LS | \vec{L} \cdot \vec{S} | k; JM_J; LS \rangle$$

where  $\tilde{A}$  is a constant that depends on  $kLS$

Thus when restricted to a single term

$$\hat{H}_2 = \tilde{A}(kLS) \vec{L} \cdot \vec{S}$$

↑

like the g-factor

Since  $\vec{L} \cdot \vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$

$\Rightarrow$  Shift  $E_{JLS}^{(0)} = \tilde{A}(LS) \left( \frac{J(J+1) - L(L+1) - S(S+1)}{2} \right)$

where  $|L-S| \leq J \leq L+S$

the term thus splits to  $\begin{cases} 2S+1 \text{ levels if } L \geq S \\ (2L+1) \text{ levels if } S \leq L \end{cases}$

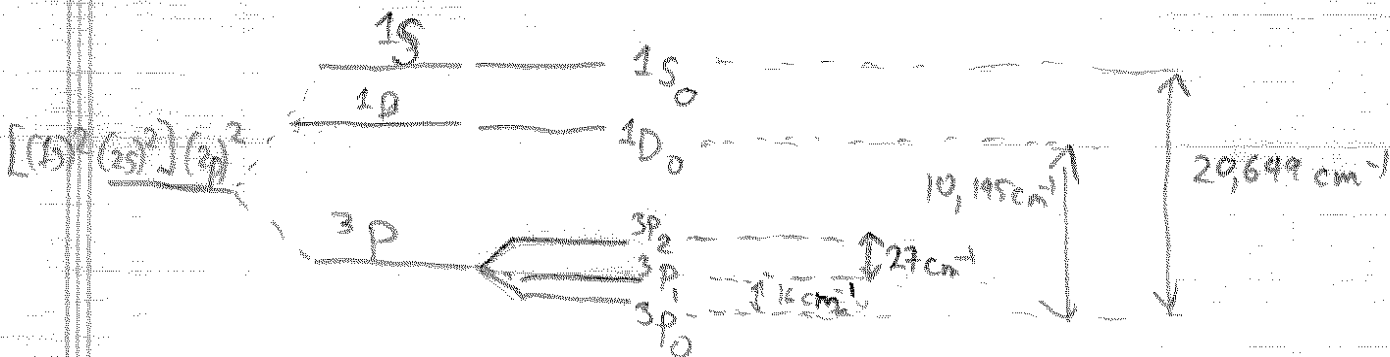
If  $\tilde{A} > 0$  the lower J have lower energy (normal multiplet)

For  $\tilde{A} < 0$  the reverse (inverted multiplet)

One can show that for a configuration with

- less than half filled subshell  $\Rightarrow \tilde{A} > 0$
- more than " " "  $\Rightarrow \tilde{A} < 0$
- half-filled  $\Rightarrow \tilde{A} = 0 \Rightarrow$  No fine structure

Ex Carbon



Lande Interval Rule: Splitting between adjacent fine structure

$E(J) - E(J-1) = \tilde{A}J$

## J-J Coupling

As discussed, for very high  $Z$ , and few electrons in a shell, spin-orbit can dominate over residual electron-electron repulsion. We thus diagonalize first  $H_0' + H_2$  then add  $H_1'$  as a perturbation.

$$H_0' + H_2 = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 + V_{\text{Coulomb}}(r_i) + \xi(r_i) \vec{l}_i \cdot \vec{s}_i \right)$$

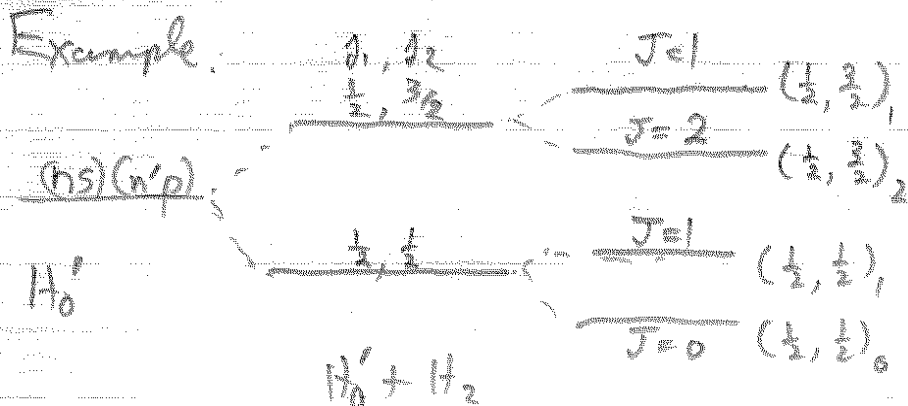
At this level,  $H = \sum_i h_i$ , where  $h_i$  are single electron Hamiltonians with single particle states on coupled orbital-spin angular momentum  $|n_i l_i s_i m_{j_i}\rangle$

The energy depends on  $E = \sum_i E_{n_i l_i s_i}$  with  $n_i l_i$

fixed in an electron configuration.

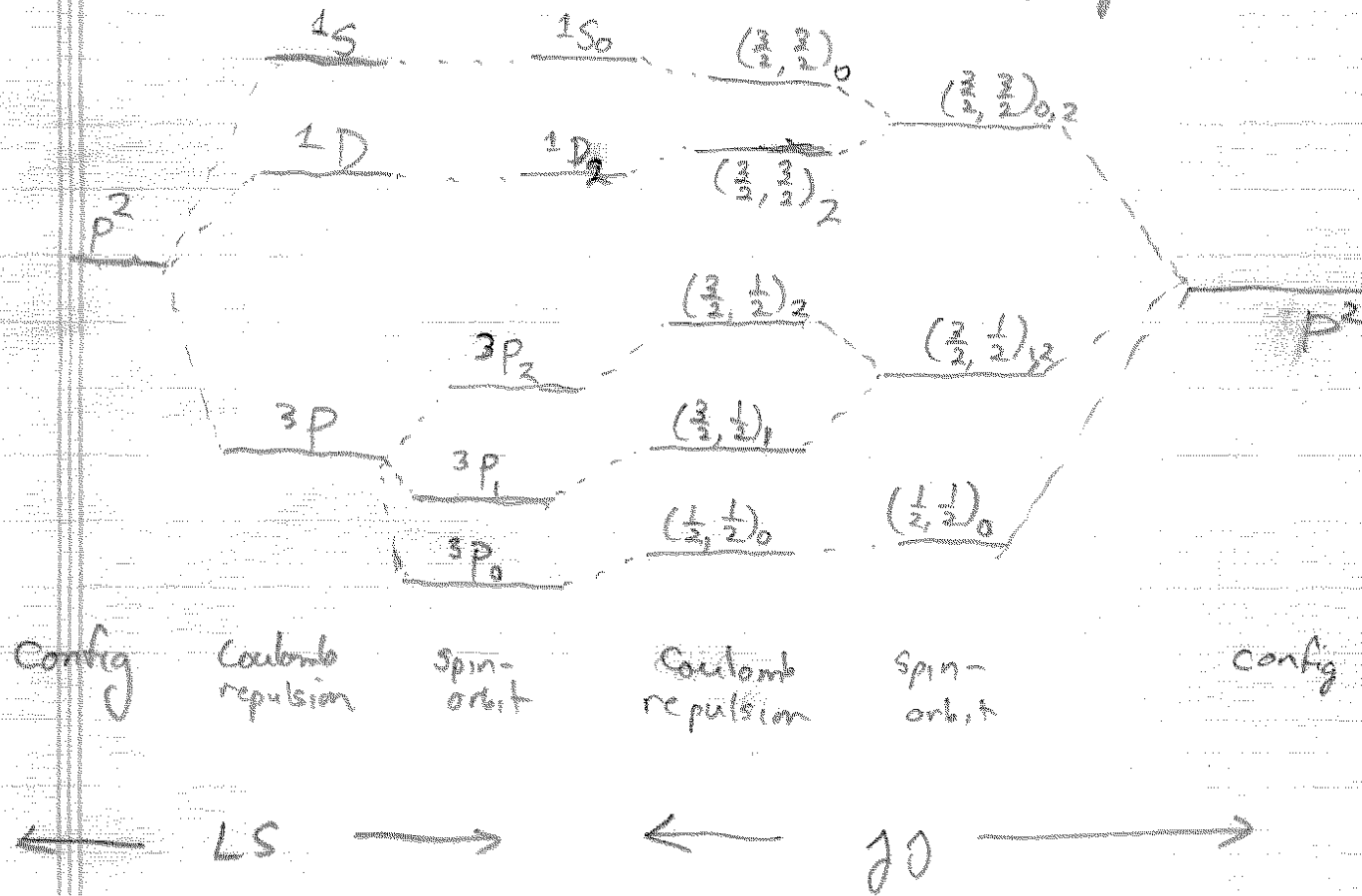
The electrons are coupled together through the Coulomb interaction where  $J, M_J$  are the good quantum numbers.

The states are denoted by the set of  $\{j_i\}$  and total  $J$



For equivalent electrons, we must take into the Pauli principle

In most cases of, even for high-Z, neither L-S or j-j coupling is dominant and ~~some~~ some form of "intermediate coupling" is required. This is accomplished by mixing together different terms as seen in a "correlation diagram".



States with unique J quantum numbers are uniquely correlated; e.g.  $3P_1 = \left(\frac{3}{2}, \frac{1}{2}\right)_1$

For  $\left(\frac{1}{2}, \frac{1}{2}\right)_0$  it is dominantly  $3P_0$  with a very small admixture of  $1S_0$

etc.