Roadmap to the structure of *N*-electron atoms

Hydrogenic systems:

- Quantum defect ✓

2-electron systems:

- Perturbation treatment - very crude ✓
- Antisymmetric wavefunctions - very important ✓

***N*-electron systems:**

- Central field approximation
- Configurations ✓
- The periodic table of elements

***LS*-coupling:**

- Detailed energy structure within a configuration

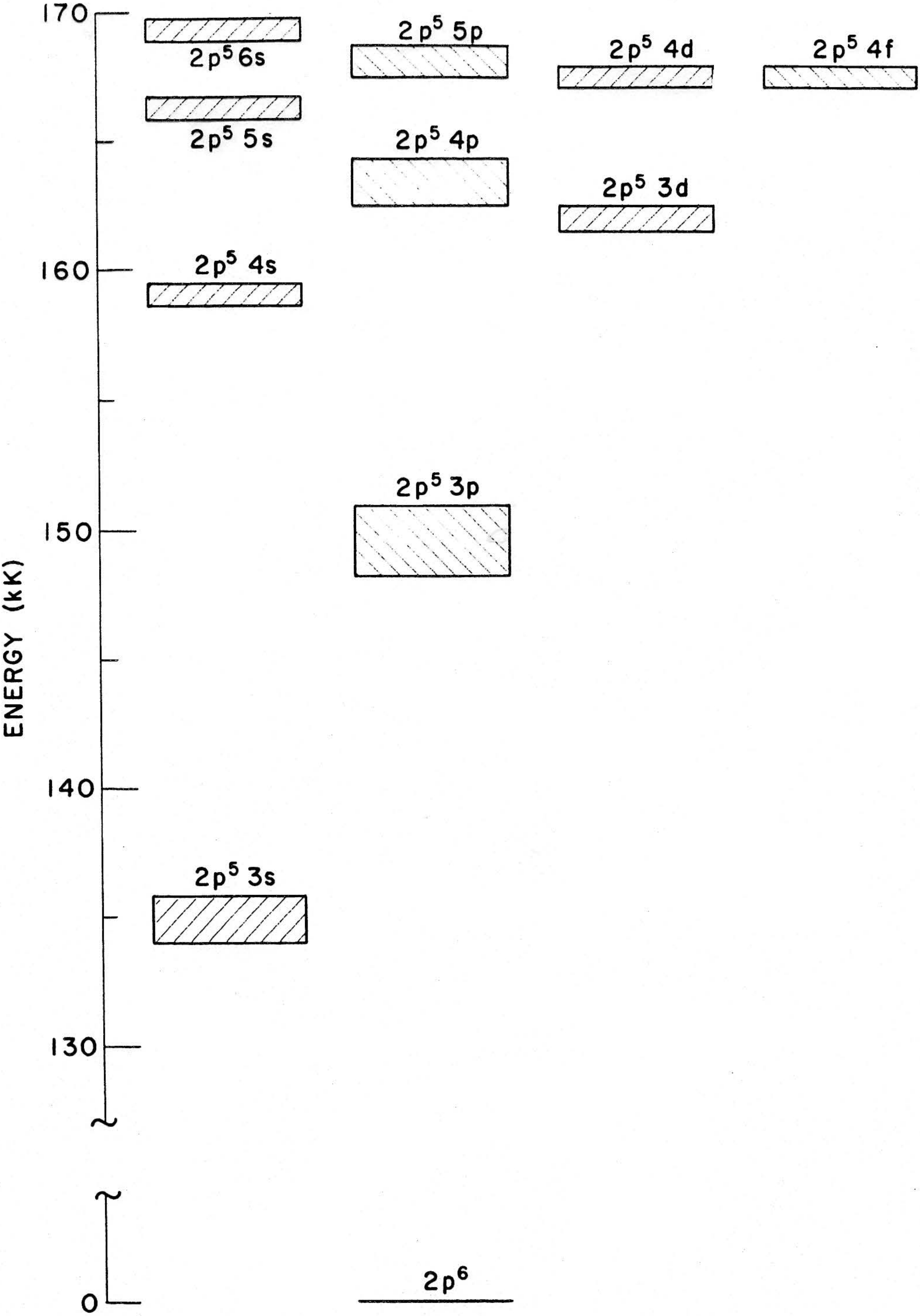


Fig. 4-1. Block diagram of the lowest configurations of Ne I. The levels of each configuration lie within the limited energy range shown by the corresponding shaded block. (There is one level in $2p^6$, and there are four levels in each p^5s configuration, ten levels in each p^5p, and twelve levels in each p^5d or p^5f configuration.)

Angular momentum

Classical

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

$$\frac{d\mathbf{L}}{dt} = \boldsymbol{\tau} = \mathbf{r} \times \mathbf{F}$$

L conserved / constant of the motion if: $\begin{cases} 1: \ \mathbf{F} = 0 \\ 2: \ \mathbf{F} \parallel \mathbf{r} \ \text{i.e. central forces} \end{cases}$

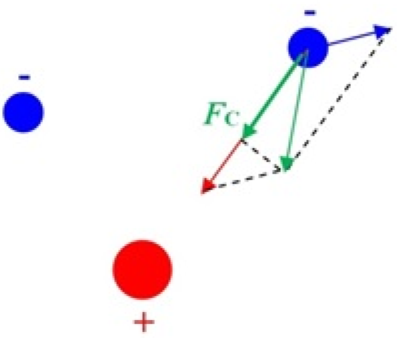
Quantum mechanical

$\hat{\mathrm{L}}$ constant of the motion $\Leftrightarrow \dfrac{d}{dt} < \hat{\mathrm{L}} >= 0 \Leftrightarrow [\hat{\mathrm{H}}, \hat{\mathrm{L}}] = 0$ (Ohlén p. 120)

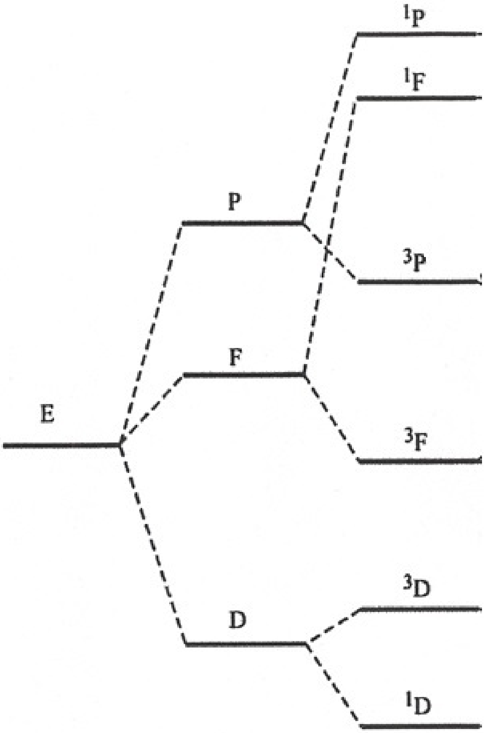
Central field approximation:

<u>Each</u> electron moves in a central field => $\hat{\ell}_i, \ i = 1, 2, ...N$ conserved

This is not true when the non-central part of the electrostatic repulsion is taken into account!



pd-configuration LS-coupling



Configuration **Term**

Central field **Repulsion**

Numerical example for 2p3d in O V, energies in cm^{-1}

E(2p3d) = 701810 Kinetic and central part of electrostatic

ΔE (P - D) = 8980 Direct part of electrostatic repulsion

ΔE (^{1}F - ^{3}F) = 15074 Exchange part of electrostatic repulsion

An explicit, LS-coupled, non antisymetrized wave function for a 2 electron configuration, $n_1 l_1 n_2 l_2$

$$
\begin{gathered}
\left|LM_L SM_S\right\rangle = \sum_{m_{\ell_1} m_{\ell_2}} \sum_{m_{s_1} m_{s_2}} \\
C(\ell_1 m_{\ell_1} \ell_2 m_{\ell_2} : LM_L)\cdot C(s_1 m_{s_1} s_2 m_{s_2} : SM_S) \\
R_{n_1\ell_1}(r_1) Y_{\ell_1 m_{\ell_1}}(\theta_1,\varphi_1)\chi_{s_1 m_{s_1}}(s_{z_1})\cdot R_{n_2\ell_2}(r_2) Y_{\ell_2 m_{\ell_2}}(\theta_2,\varphi_2)\chi_{s_2 m_{s_2}}(s_{z_2})
\end{gathered}
$$

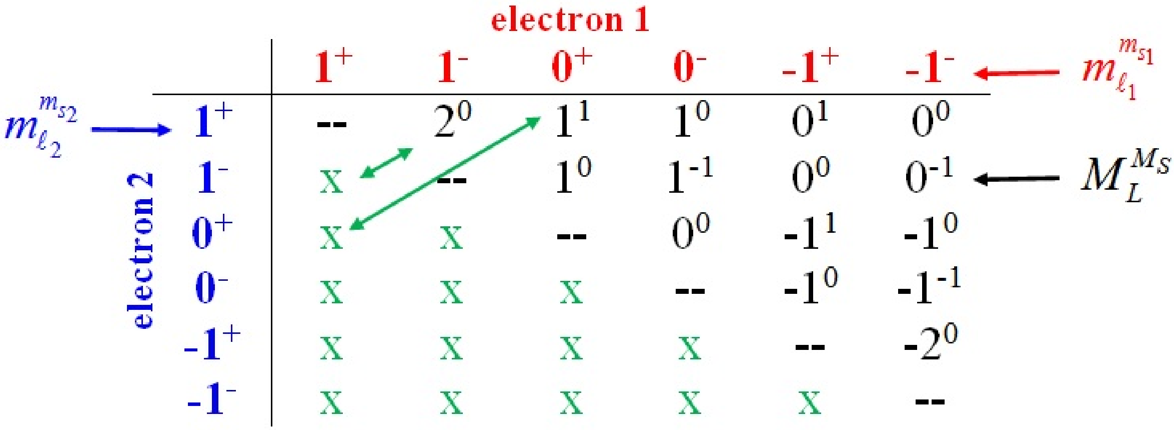
Numerical

Equivalent electrons, p^2 configuration.

The table shows $M_L^{M_S}$ where $M_L = m_{l_1} + m_{l_2}$ and $M_S = m_{s_1} + m_{s_2}$.

--: Marks the "diagonal" where all quantum numbers would be equal, which is not possible for antisymmetric wavefunctions (Pauli principle).

x: Marks states indistinguishable from states above the diagonal which means that both cannot exist.



	1^+	1^-	0^+	0^-	-1^+	-1^-
1^+	--	2^0	1^1	1^0	0^1	0^0
1^-	x	--	1^0	1^{-1}	0^0	0^{-1}
0^+	x	x	--	0^0	-1^1	-1^0
0^-	x	x	x	--	-1^0	-1^{-1}
-1^+	x	x	x	x	--	-2^0
-1^-	x	x	x	x	x	--

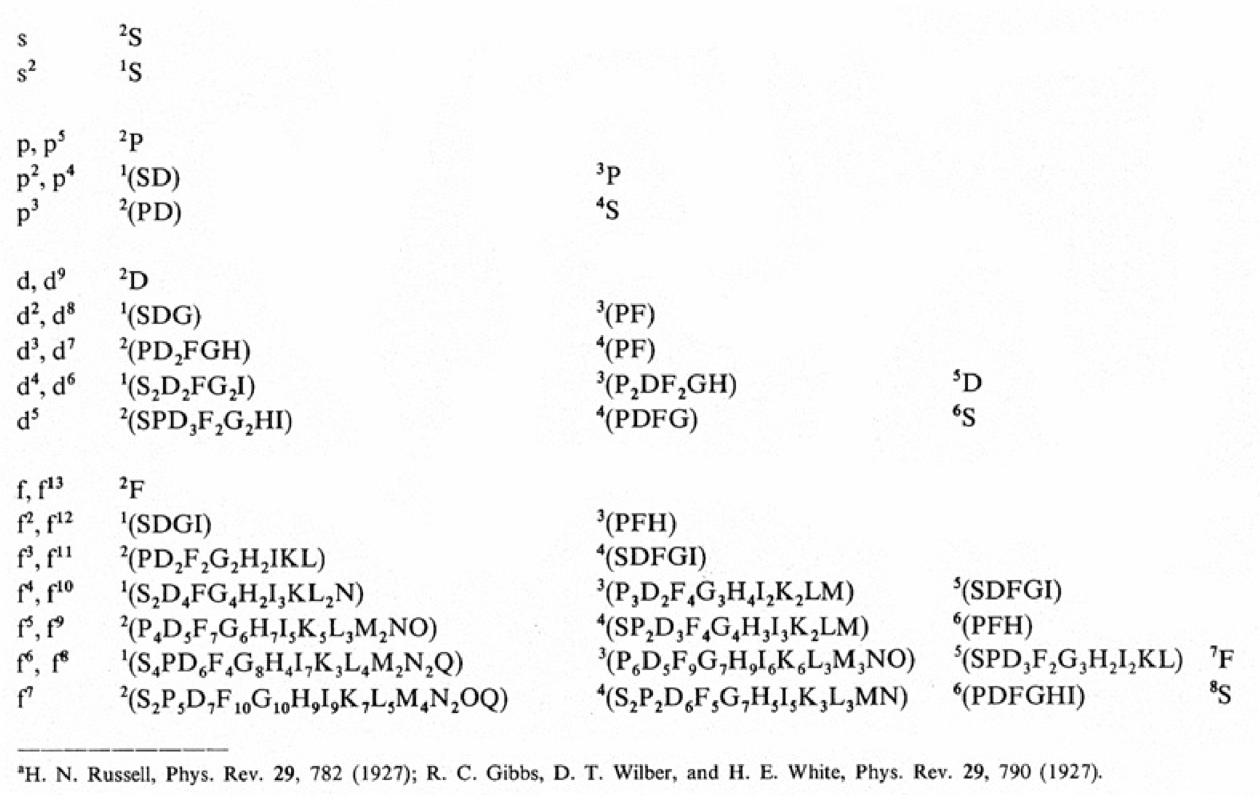
The allowed combinations correspond exactly to the *LS*-terms ^{1}D, ^{1}S and ^{3}P, which are thus the only possible ones in a p^2 configuration.

For a general 2-electron configuration $n\ell^2$ it can be shown that the allowed *LS* terms are those for which:

$$\boxed{L + S \text{ is an even number}}$$

Permitted LS-terms with equivalent electrons

Note: electrons and holes, e.g p^2 and p^4, give the same *LS* terms



s	^2S			
s^2	^1S			
p, p^5	^2P			
p^2, p^4	$^1(SD)$	^3P		
p^3	$^2(PD)$	^4S		
d, d^9	^2D			
d^2, d^8	$^1(SDG)$	$^3(PF)$		
d^3, d^7	$^2(PD_2FGH)$	$^4(PF)$		
d^4, d^6	$^1(S_2D_2FG_2I)$	$^3(P_2DF_2GH)$	^5D	
d^5	$^2(SPD_3F_2G_2HI)$	$^4(PDFG)$	^6S	
f, f^{13}	^2F			
f^2, f^{12}	$^1(SDGI)$	$^3(PFH)$		
f^3, f^{11}	$^2(PD_2F_2G_2H_2IKL)$	$^4(SDFGI)$		
f^4, f^{10}	$^1(S_2D_4FG_4H_2I_3KL_2N)$	$^3(P_3D_2F_4G_3H_4I_2K_2LM)$	$^5(SDFGI)$	
f^5, f^9	$^2(P_4D_5F_7G_6H_7I_5K_5L_3M_2NO)$	$^4(SP_2D_3F_4G_4H_3I_3K_2LM)$	$^6(PFH)$	
f^6, f^8	$^1(S_4PD_6F_4G_8H_4I_7K_3L_4M_2N_2Q)$	$^3(P_6D_5F_9G_7H_9I_6K_6L_3M_3NO)$	$^5(SPD_3F_2G_3H_2I_2KL)$	^7F
f^7	$^2(S_2P_5D_7F_{10}G_{10}H_9I_9K_7L_5M_4N_2OQ)$	$^4(S_2P_2D_6F_5G_7H_5I_5K_3L_3MN)$	$^6(PDFGHI)$	^8S

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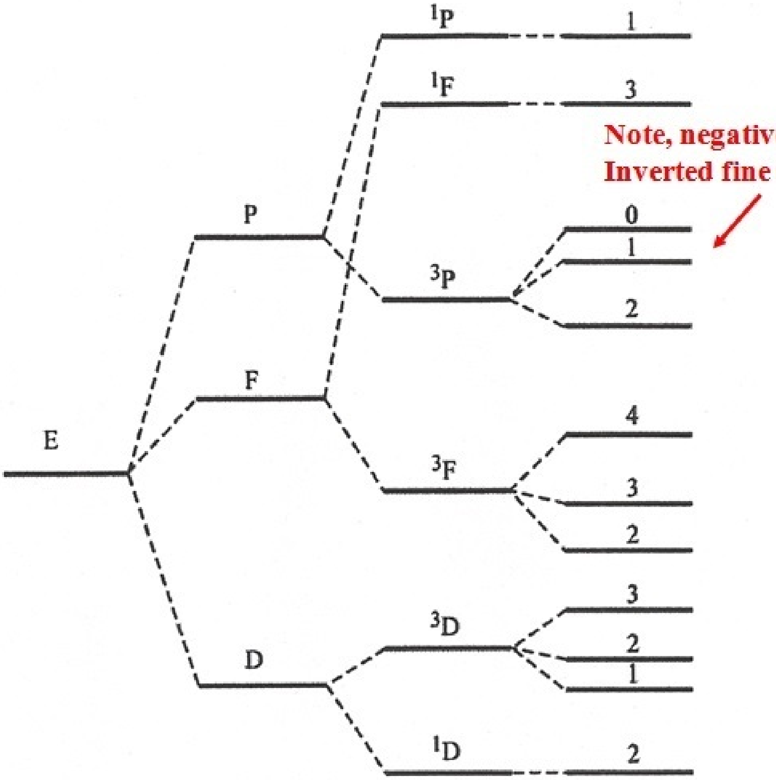
[a] H. N. Russell, Phys. Rev. 29, 782 (1927); R. C. Gibbs, D. T. Wilber, and H. E. White, Phys. Rev. 29, 790 (1927).

pd-configuration LSJ-coupling



Note, negative β.
Inverted fine structure

Configuration **Term** **Level**

Central field **Repulsion** **Spin-orbit**

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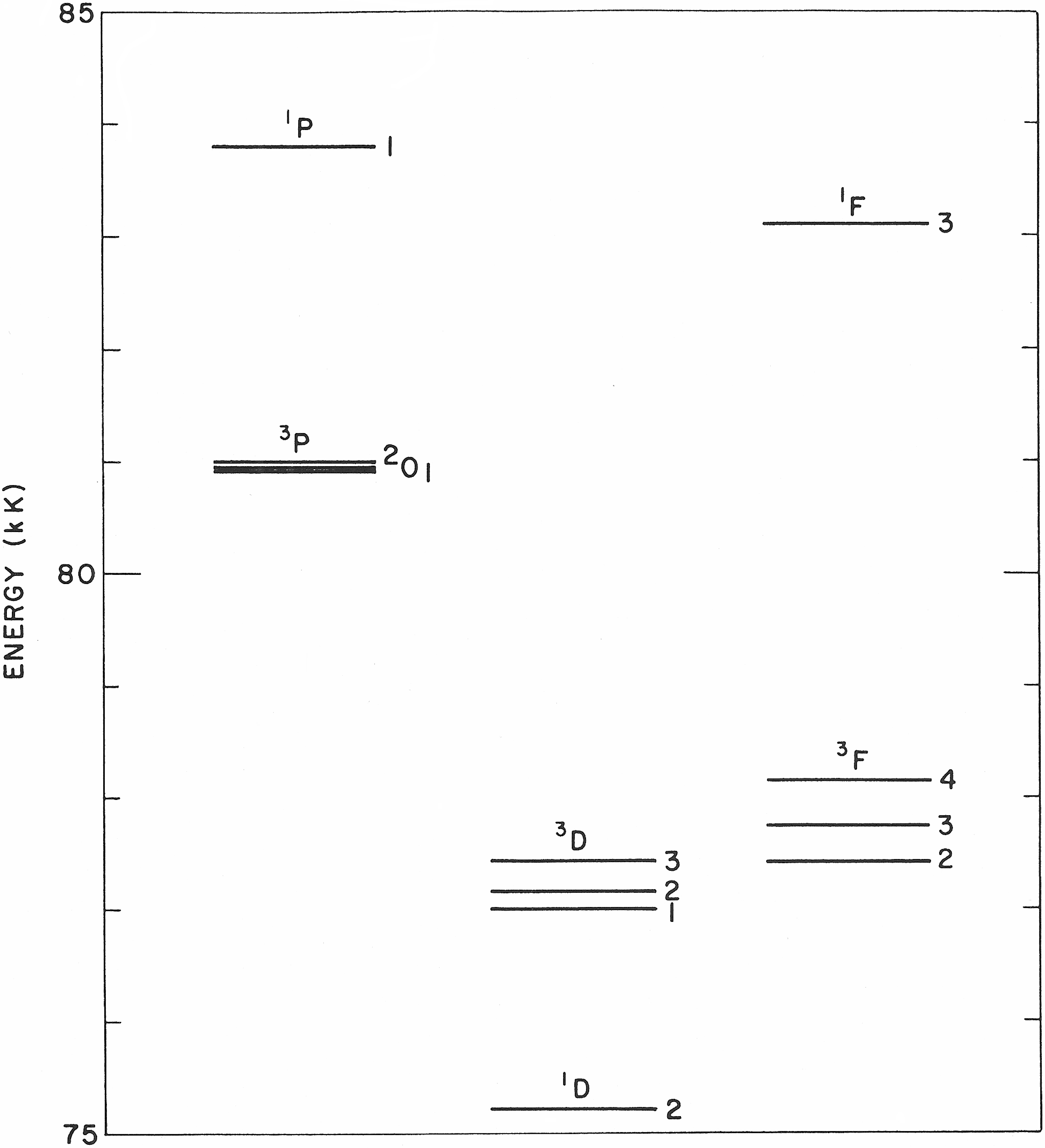
ΔE (P - D) =	8980	Direct part of electrostatic repulsion
ΔE (^{1}F - ^{3}F) =	15074	Exchange part of electrostatic repulsion
ΔE ($^3F_4$- $^3F_3$) =	235	Spin-orbit magnetic energy



The observed energy levels of the configuration Ti III 3d4p.

Selection rules E1 (electric dipole) transitions

Foot 2.26: Rate $\propto \left|e\overline{E}_0\right|^2 \cdot \left|\int \Psi_2 (\hat{r} \cdot \overline{e}_{\text{rad}}) \Psi_1 \, d^3 r\right|^2$

$\Delta J = 0, \pm 1$ not 0 to 0

Only one electron can change orbital, i.e. $n\ell$.

Highly unlikely that two electrons would rearrange themselves simultaneously

$\hat{r} =$ one-electron operator

$\Delta \ell = \pm 1$

$\hat{r}$ has odd parity and $Y_{\ell,m}(\theta,\varphi)$ has $(-1)^{\ell}$

If perfect *LS*-coupling

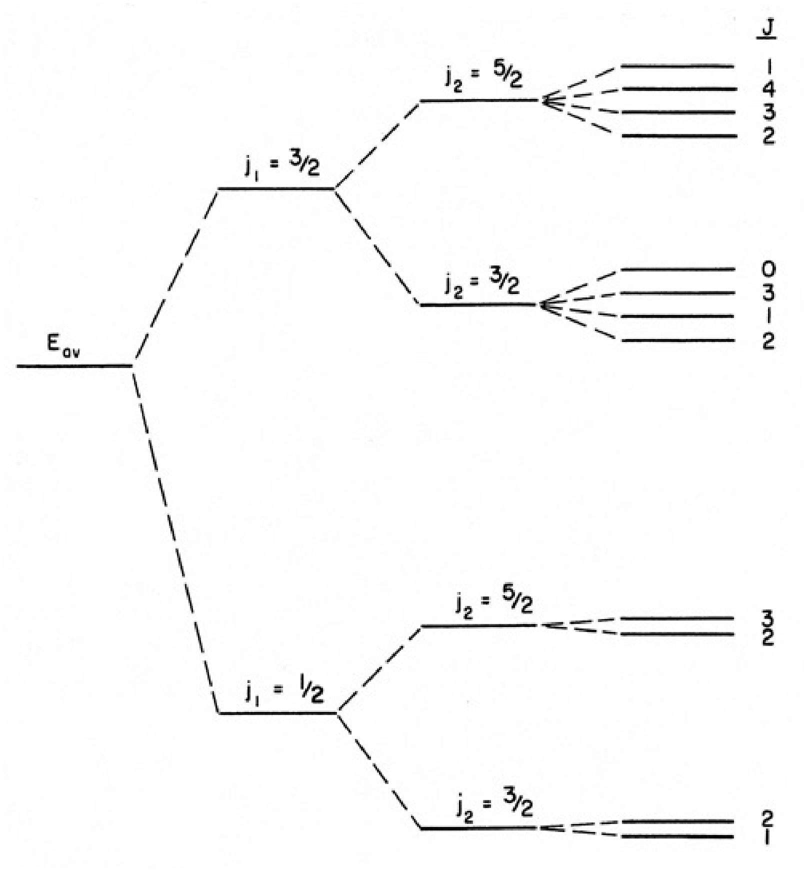
$\Delta S = 0$

$\hat{r}$ does not include spin, thus can't change it

$\Delta L = 0, \pm 1$ not 0 till 0

Follows from ΔJ and ΔS

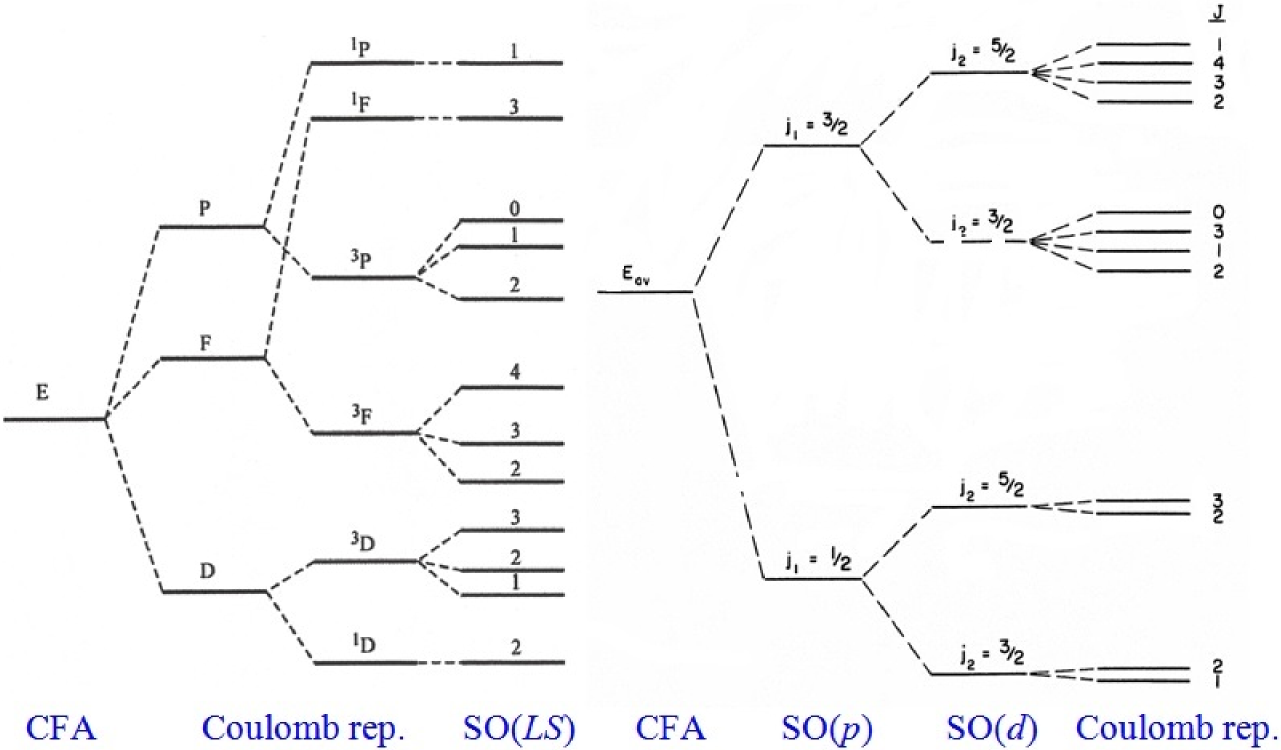
pd configuration in *jj*-coupling



Configuration **SO(p)** **SO(d)** **Coulomb rep.**

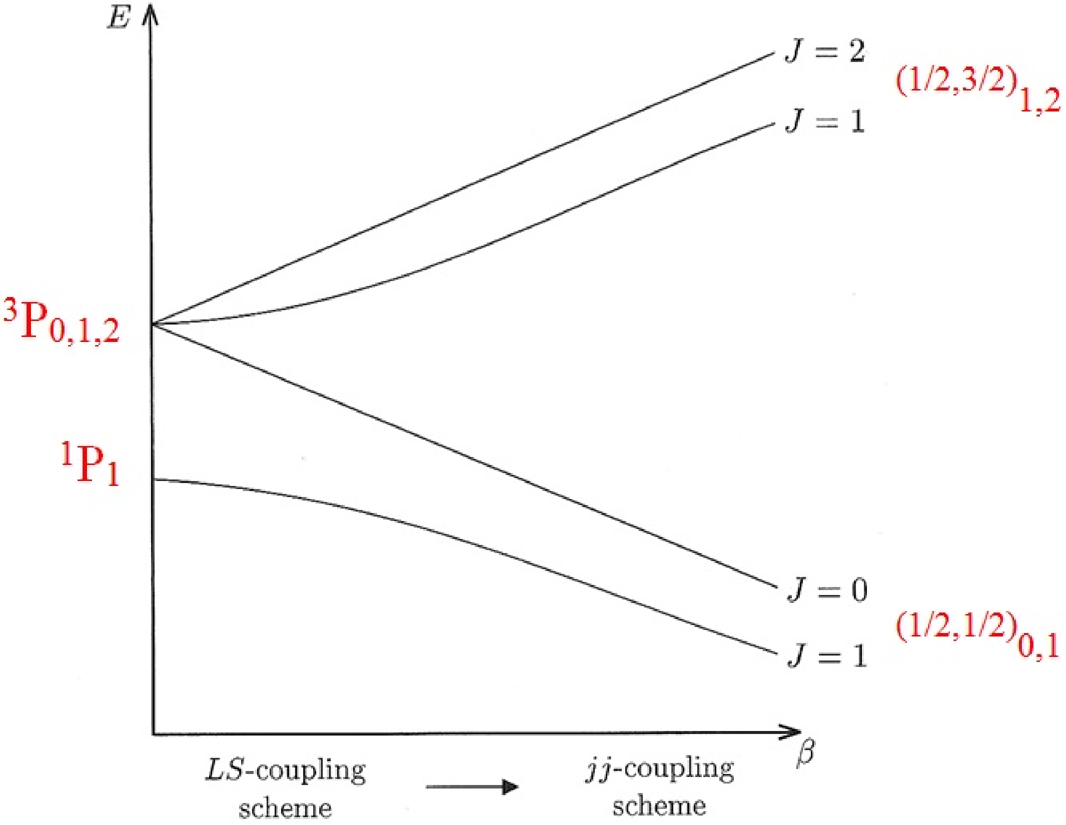
Same number of energy levels and the same total *J* as in *LS*-coupling. Only our <u>names</u> of the levels have changed.

pd-configuration LSJ and jj - coupling



Same number of energy levels and the same total *J*.
Only our names of the levels have changed.

LS to *jj* - coupling transition in a sp-configuration. Foot Fig. 5.10

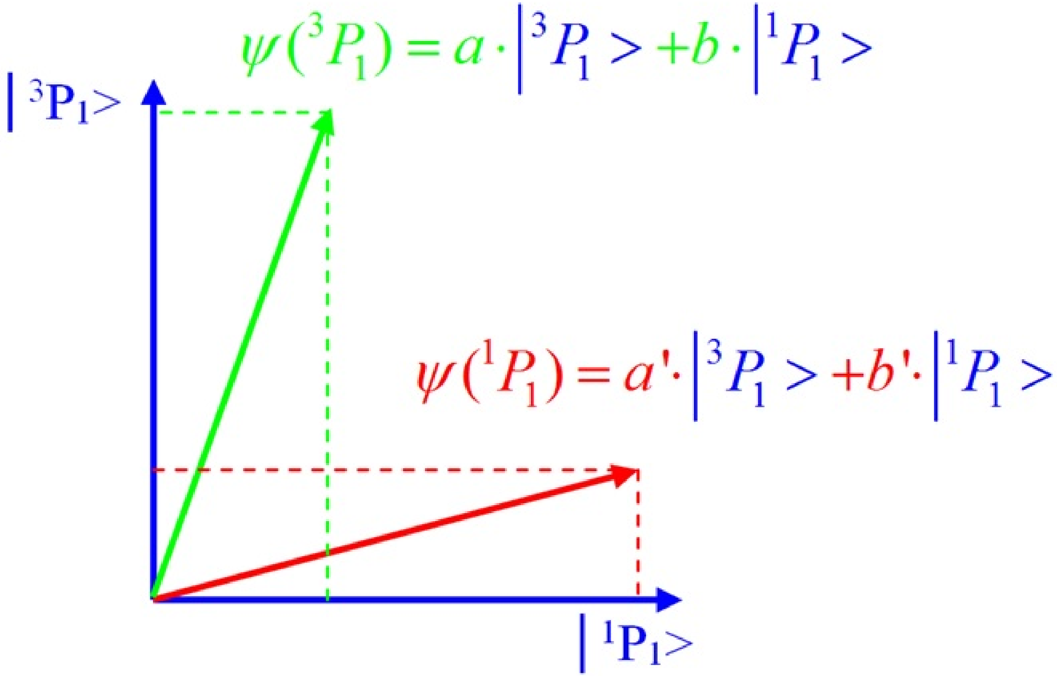


Relative energies as a function of the spin-orbit parameter, β.

Note how the 2 $J = 1$ states seems to "repel" each other while the two unique J-values (0 and 2) just increase linearly with the β-parameter.

Intermediate coupling in a sp configuration

The “physical” levels that we name or label $^3P_1$ and $^1P_1$ can be written as linear combinations of the *LS*-coupled basis functions. If a >> b then $^3P_1$ has properties very close to those of the basis function $|^3P_1>$. If, on the other hand a ≈ b then it behaves both like a singlet and a triplet.



$$\psi(^3P_1) = a \cdot |^3P_1 > + b \cdot |^1P_1 >$$

$$\psi(^1P_1) = a' \cdot |^3P_1 > + b' \cdot |^1P_1 >$$

$$a^2 + b^2 = 1 \text{ and } a'^2 + b'^2 = 1$$

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$\Delta J = 0, \pm 1$ not 0 to 0

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$\hat{r} =$ one-electron operator

$\Delta \ell = \pm 1$

$\hat{r}$ has odd parity and $Y_{\ell,m}(\theta,\varphi)$ has $(-1)^\ell$

If perfect *LS*-coupling

$\Delta S = 0$

$\hat{r}$ does not include spin, thus can't change it

$\Delta L = 0, \pm 1$ not 0 till 0

Follows from ΔJ and ΔS

LS or jj-basis

$$\psi(^1P_1) = a'\cdot\left|^3P_1\right> + b'\cdot\left|^1P_1\right> = a''\cdot(1/2,1/2)_1 + b''\cdot(1/2,3/2)_1$$