Ground state of $3d^N$ system

Ground state of $3d^N$ system

Hunds rules

- Term symbols with **maximum spin** S are lowest in energy,
- Among these terms:

  Term symbols with **maximum L** are lowest in energy
- In the presence of spin-orbit coupling, the lowest term has
- J = |L-S| if the shell is less than half full
- **J = L+S** if the shell is more than half full

Ground state of $3d^N$ system

max S > max L > max J (if more than half full)

What is the Hund's rule ground states for $3d^2$?

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

Ground state of $3d^N$ system

max S > max L > max J (if more than half full)

What is the Hund's rule ground states for $3d^2$?

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

L=3, S=1

J=2 Term symbol = $^3F_2$

Ground state of $3d^N$ system

max S > max L > max J (if more than half full)

What is the Hund's rule ground states for $3d^2$?

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

$$f_k = (2l_1 + 1)(2l_2 + 1)(-1)^L \begin{pmatrix} l_1 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_2 & l_1 & k \end{Bmatrix}$$

Ground state of $3d^N$ system

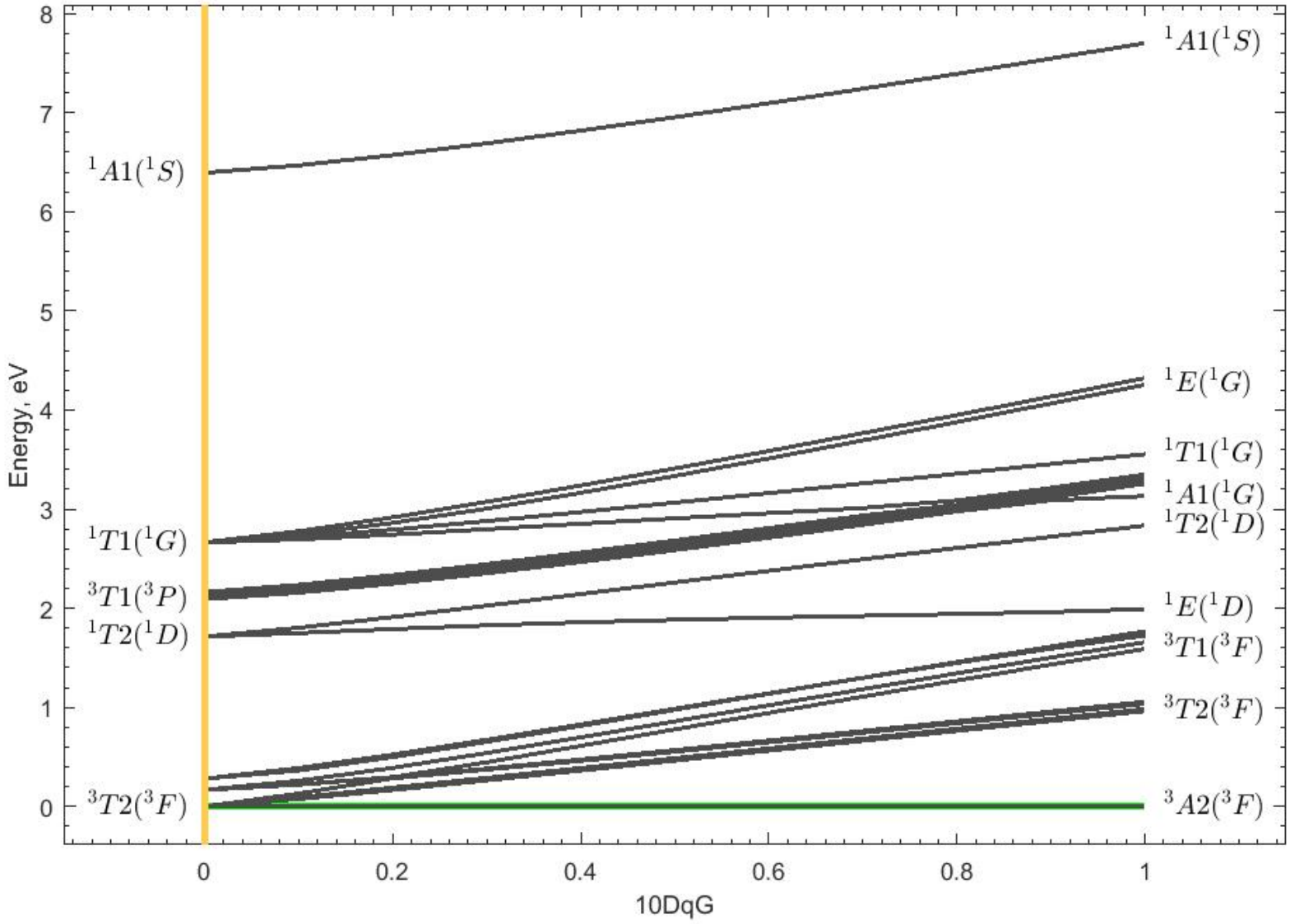
What is the Hund's rule ground states for $3d^2$?

	f_2		f_4		Energy
^1S	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 0\\ 2 & 2 & 2\end{Bmatrix}$	2/7	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 0\\ 2 & 2 & 4\end{Bmatrix}$	2/7	$0.46F^2$
^3P	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 1\\ 2 & 2 & 2\end{Bmatrix}$	3/21	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 1\\ 2 & 2 & 4\end{Bmatrix}$	–4/21	$0.02F^2$
^1D	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 2\\ 2 & 2 & 2\end{Bmatrix}$	–3/49	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 2\\ 2 & 2 & 4\end{Bmatrix}$	4/49	$-0.01F^2$
^3F	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 3\\ 2 & 2 & 2\end{Bmatrix}$	–8/49	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 3\\ 2 & 2 & 4\end{Bmatrix}$	–1/49	$-0.18F^2$
^1G	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 4\\ 2 & 2 & 2\end{Bmatrix}$	4/49	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 4\\ 2 & 2 & 4\end{Bmatrix}$	1/441	$0.08F^2$

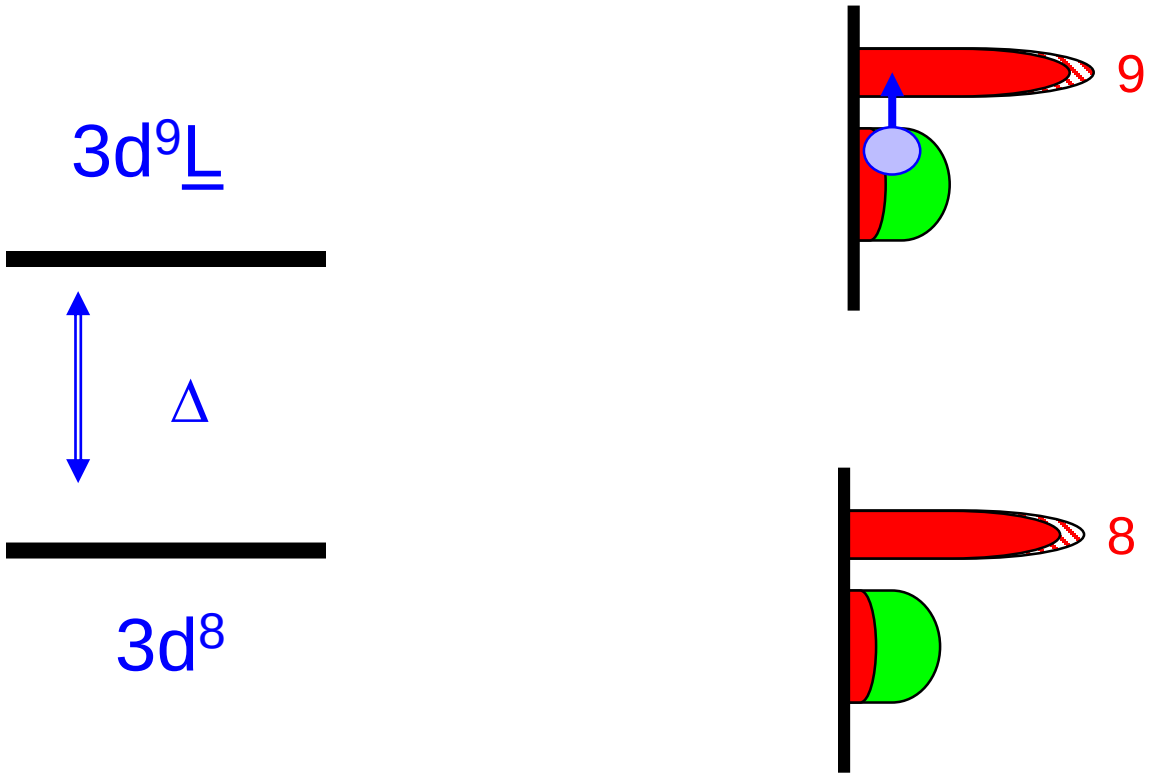
Ground state of $3d^N$ system

	Energy	Symmetries O_h	Total symmetry
^1S	4.6 eV	$^1A_1$	
^3P	0.2 eV	$^3T_1$	
^1D	-0.1 eV	$^1E + {}^1T_2$	
^3F	-1.8 eV	**$^3A_2$** $+ {}^3T_1 + {}^3T_2$	
^1G	0.8 eV	$^1A_1+{}^1T_1+{}^1T_2+{}^1E$	

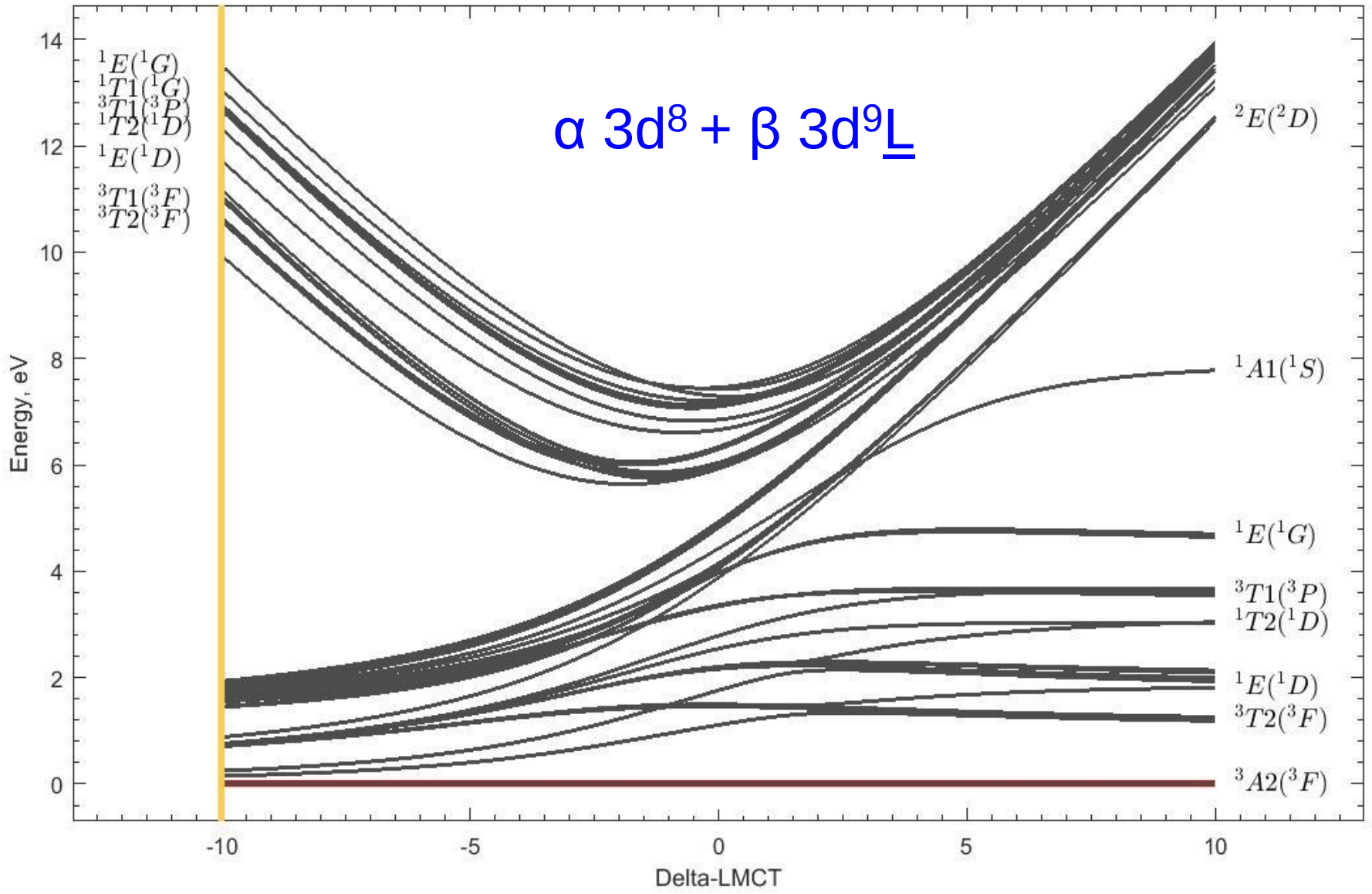
Ground state of $3d^N$ system



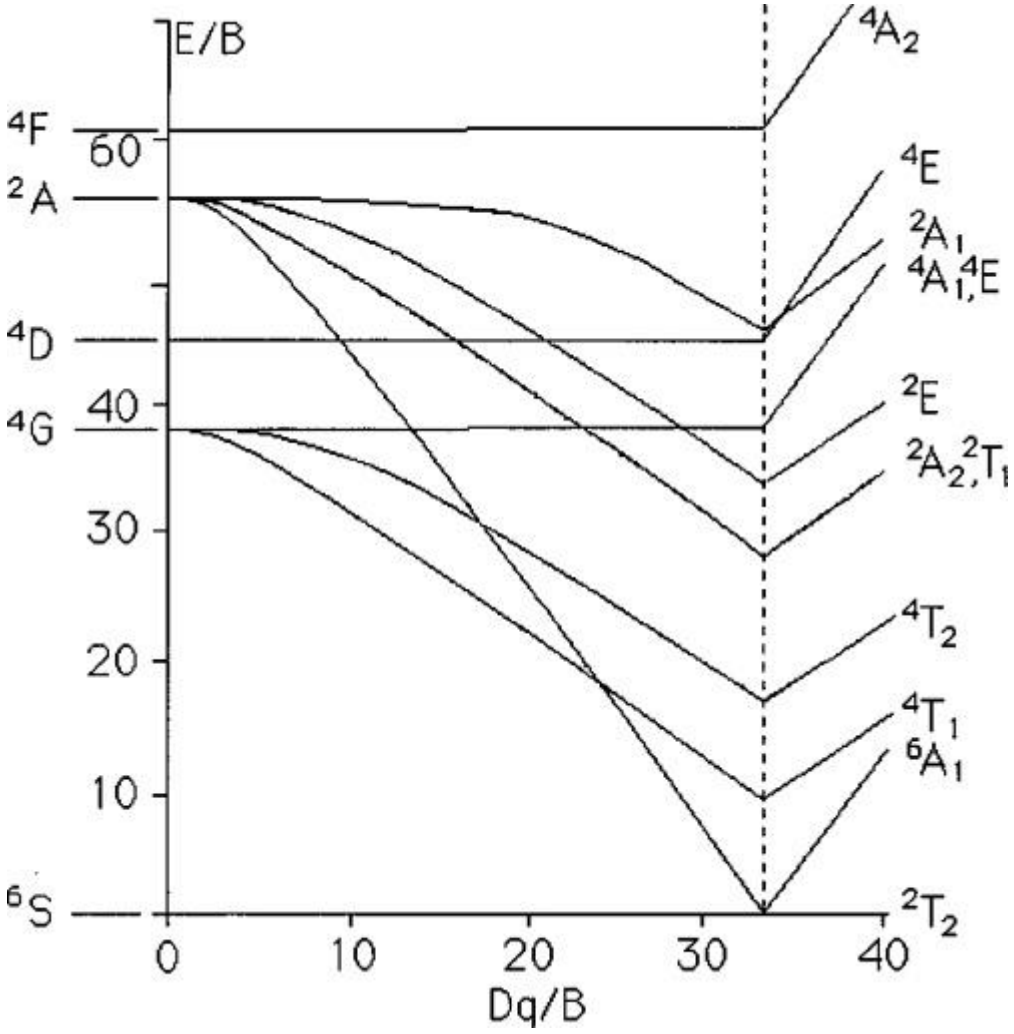
Ground state with charge transfer



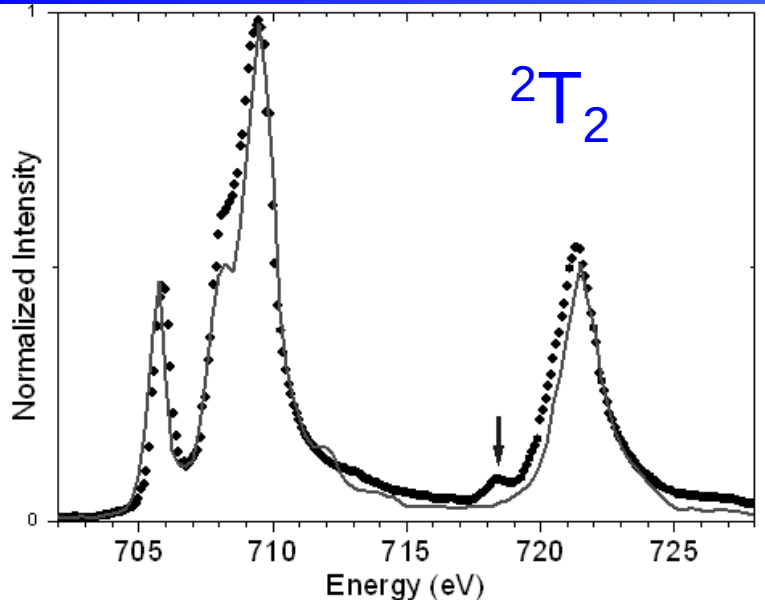
Ground state with charge transfer

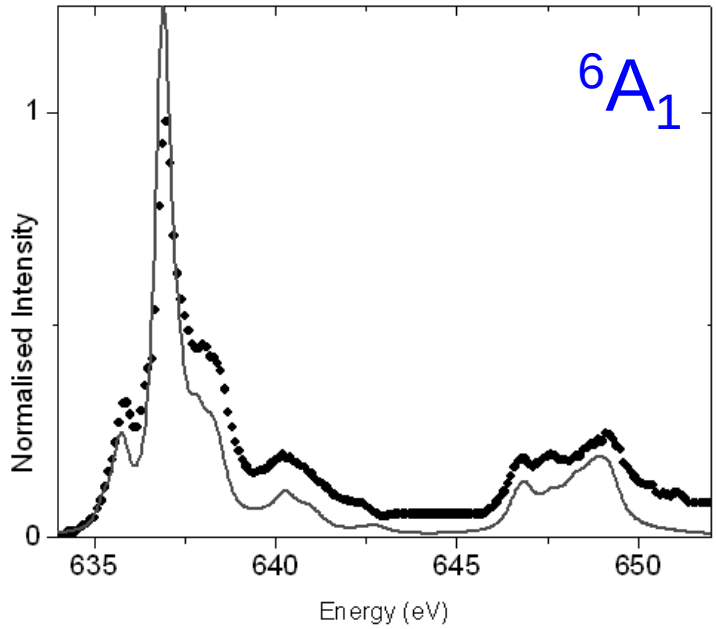


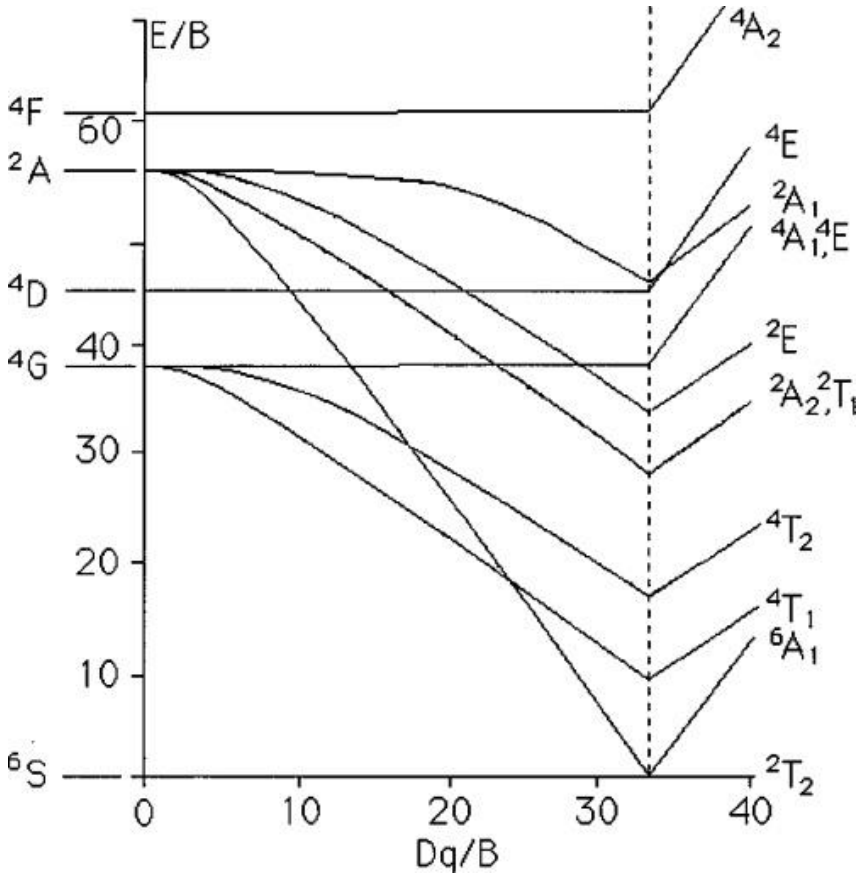
Ground state symmetry and XAS



Ground state symmetry and XAS

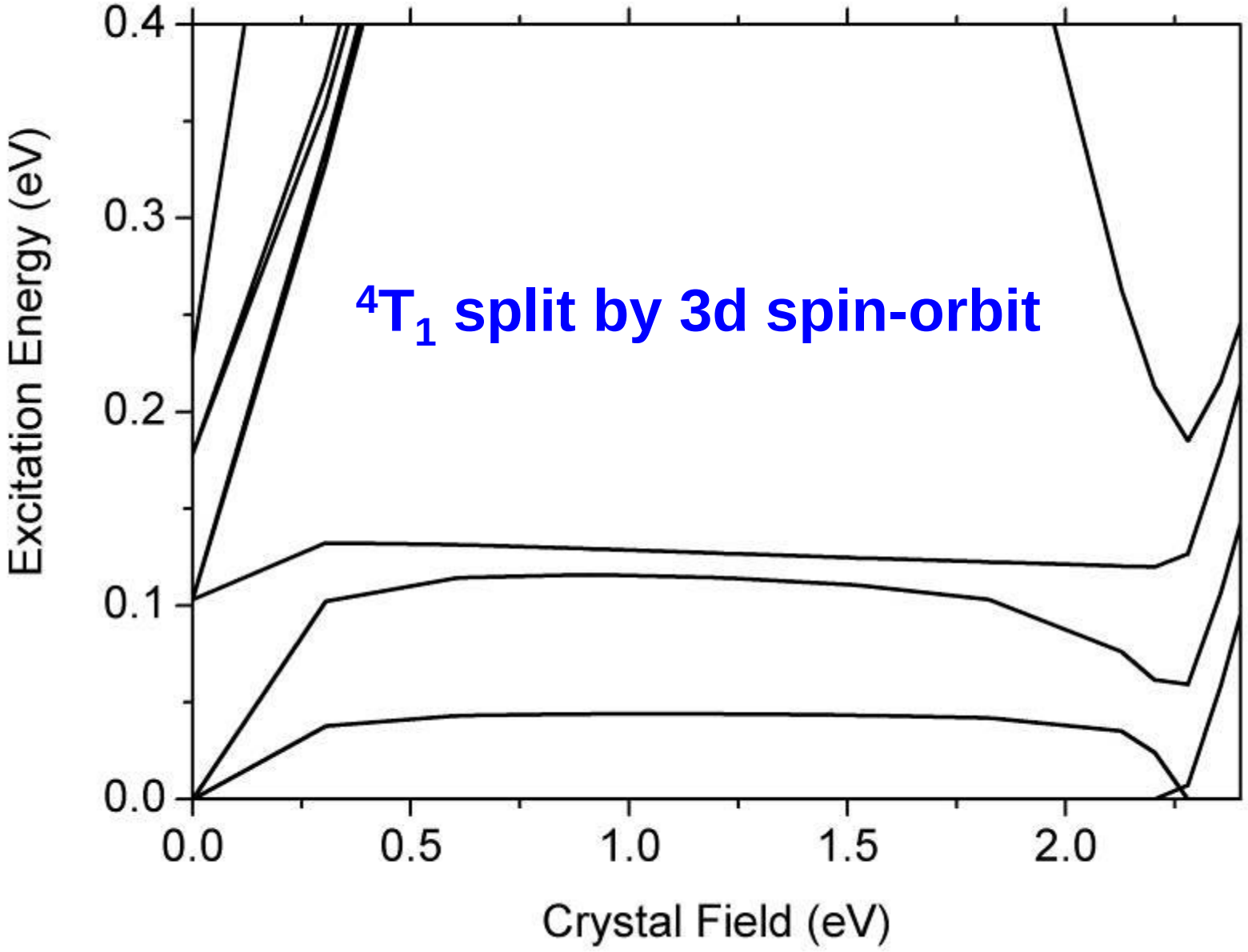




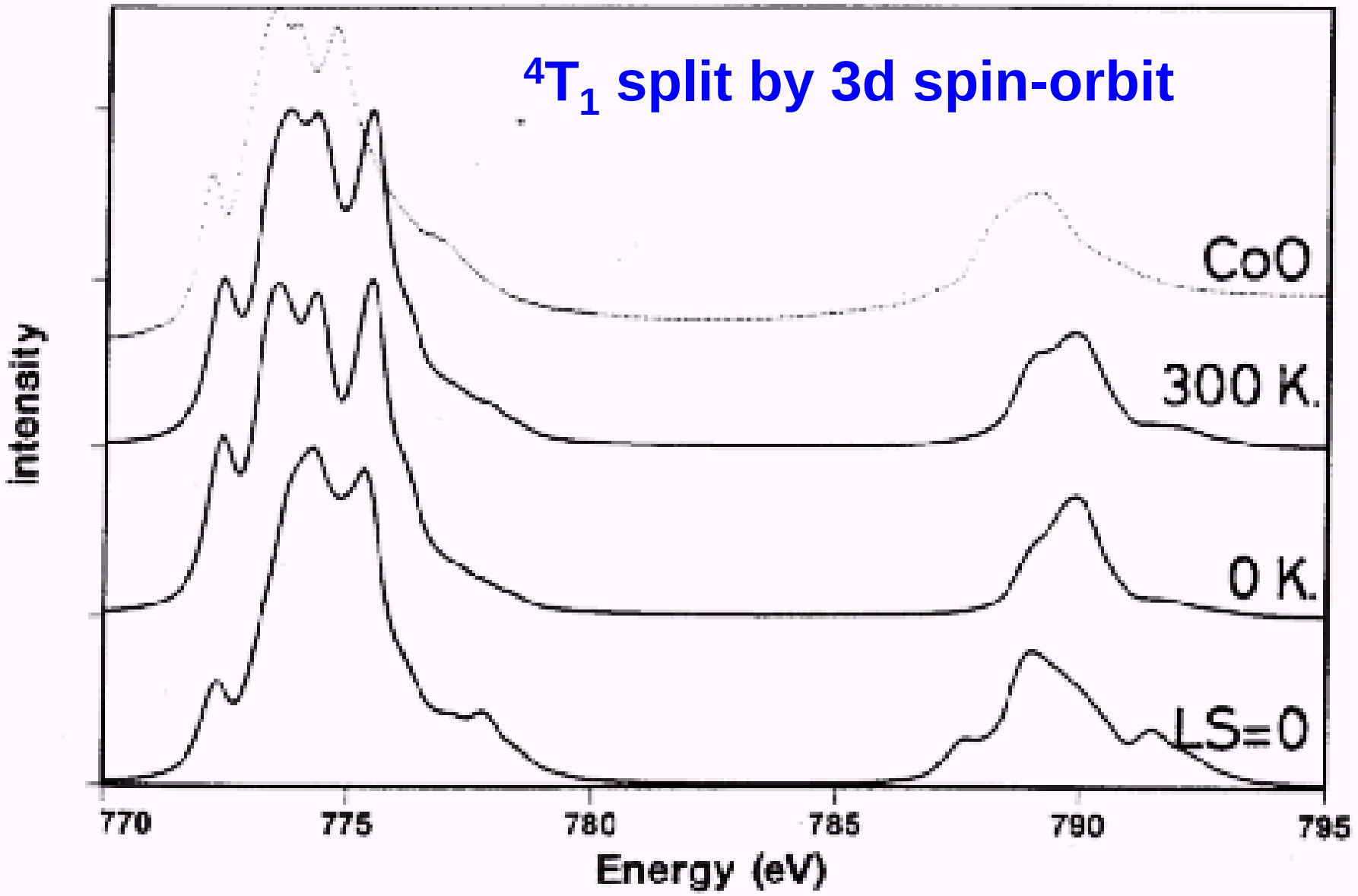


High-spin or low-spin

Ground state symmetry and XAS

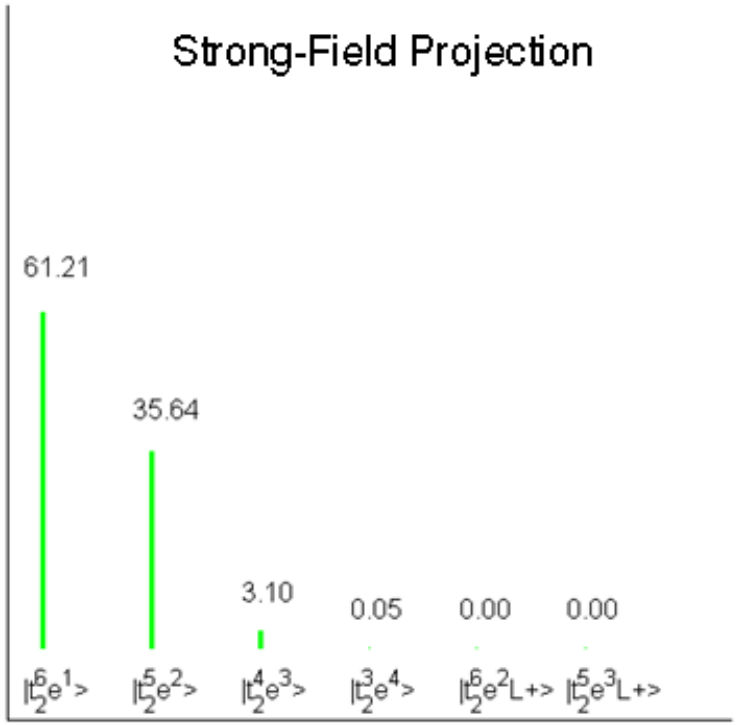


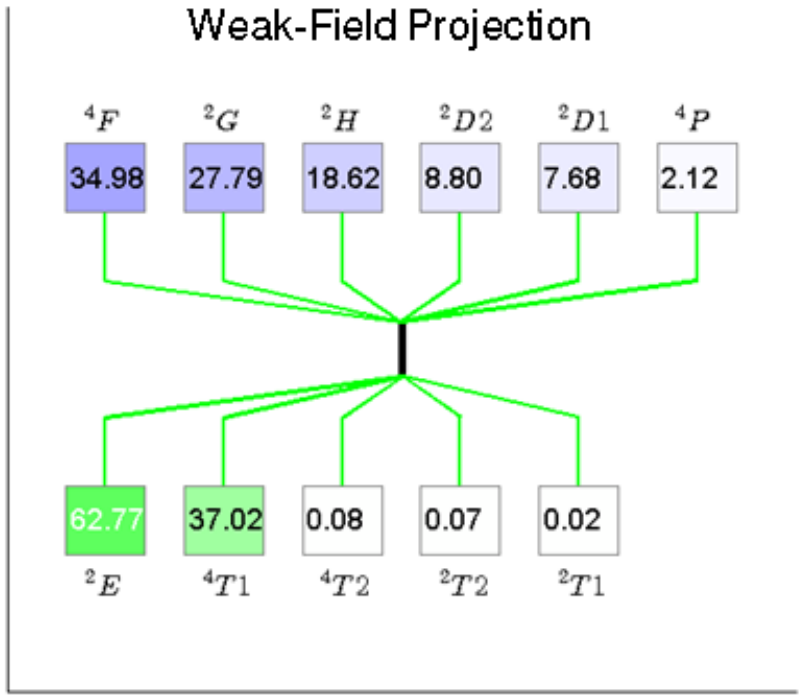
Ground state symmetry and XAS



Ground-State Projections

The following shows the strong-field (left) and the weak-field (right) projections (given as an atomic LS and O_h expansions) of the lowest energy multiplet for an octahedral Co^{2+} system with 10Dq = 2.3 eV and no reduction on the Slater Integrals.





[Delgado et al. J. Synchrot. Rad 23, 1264 (2016)]

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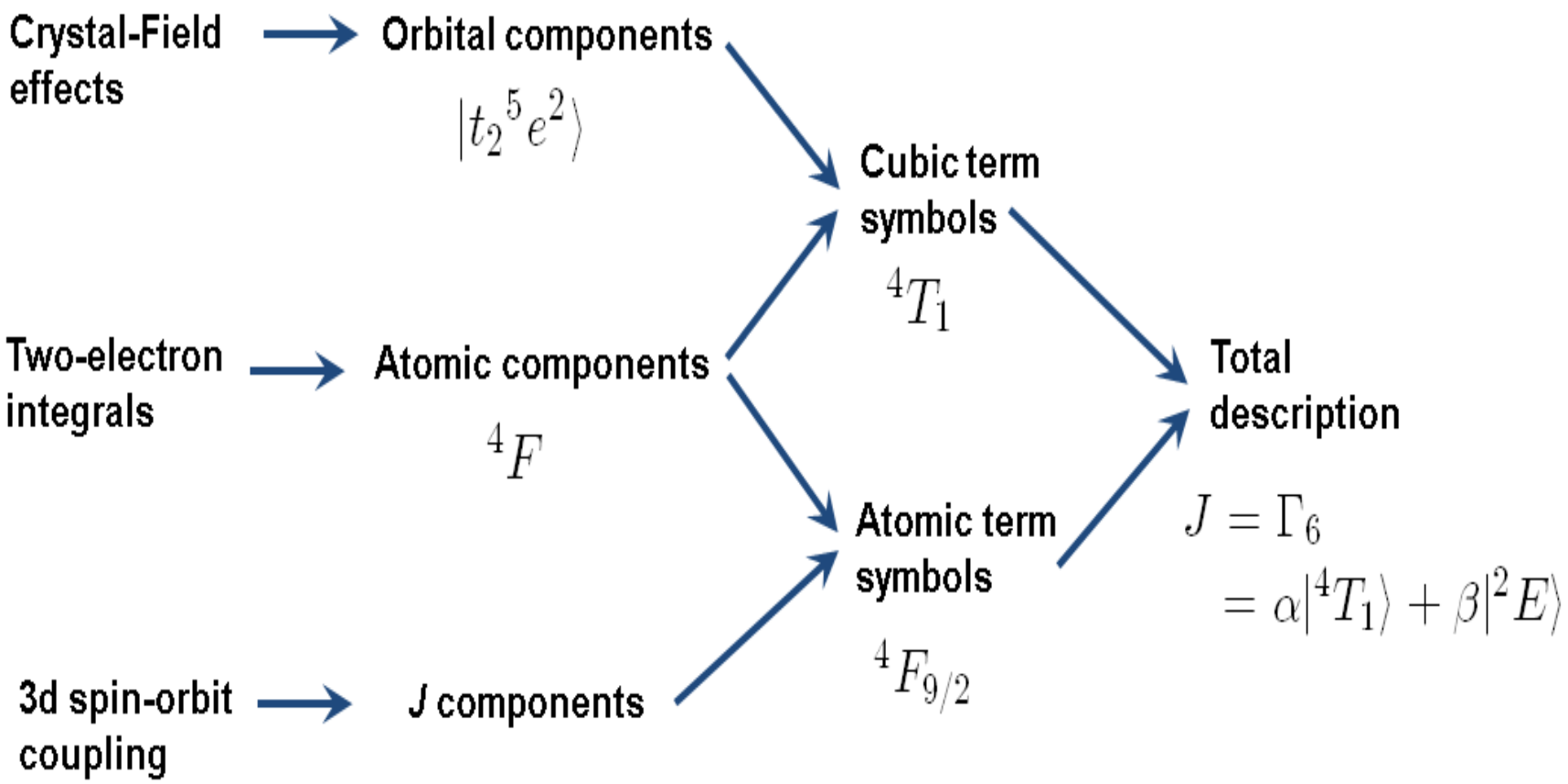

+ charge transfer
+ translation symmetry

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[Delgado et al. J. Synchrot. Rad 23, 1264 (2016)]

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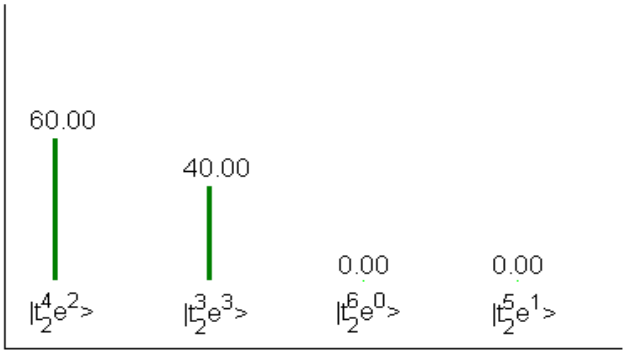
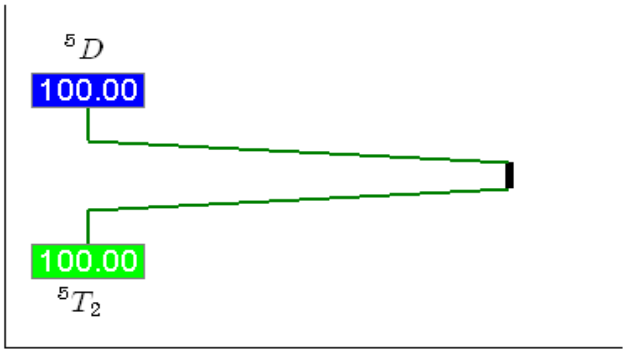
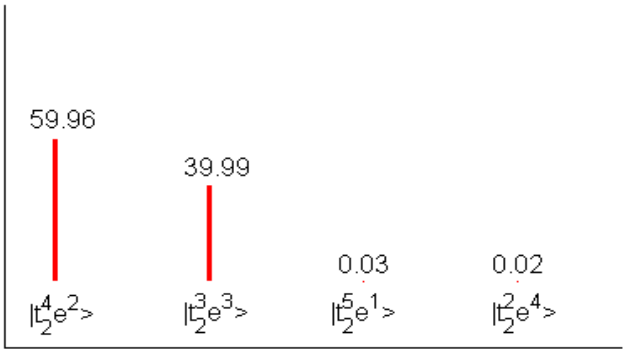
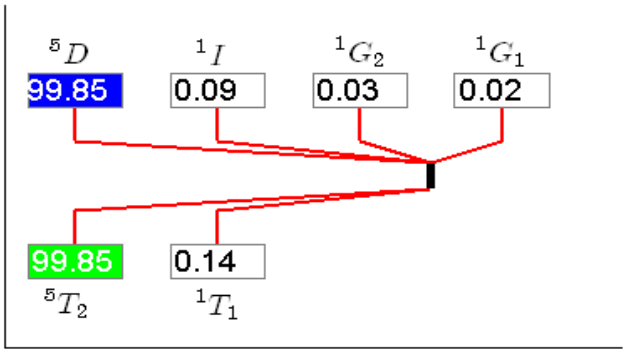


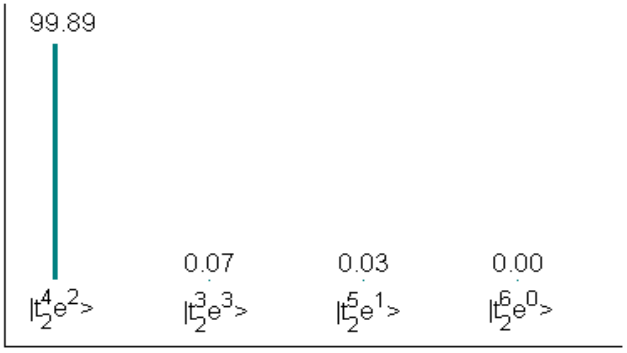
a) Fe^{2+}
10Dq = 0
SOC_{3d} = 0



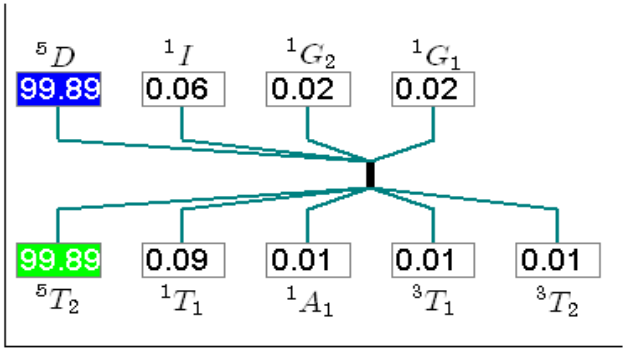


b) Fe^{2+}
10Dq = 0
Atomic SOC_{3d}





c) Fe^{2+}
10Dq = 1.3
Atomic SOC_{3d}



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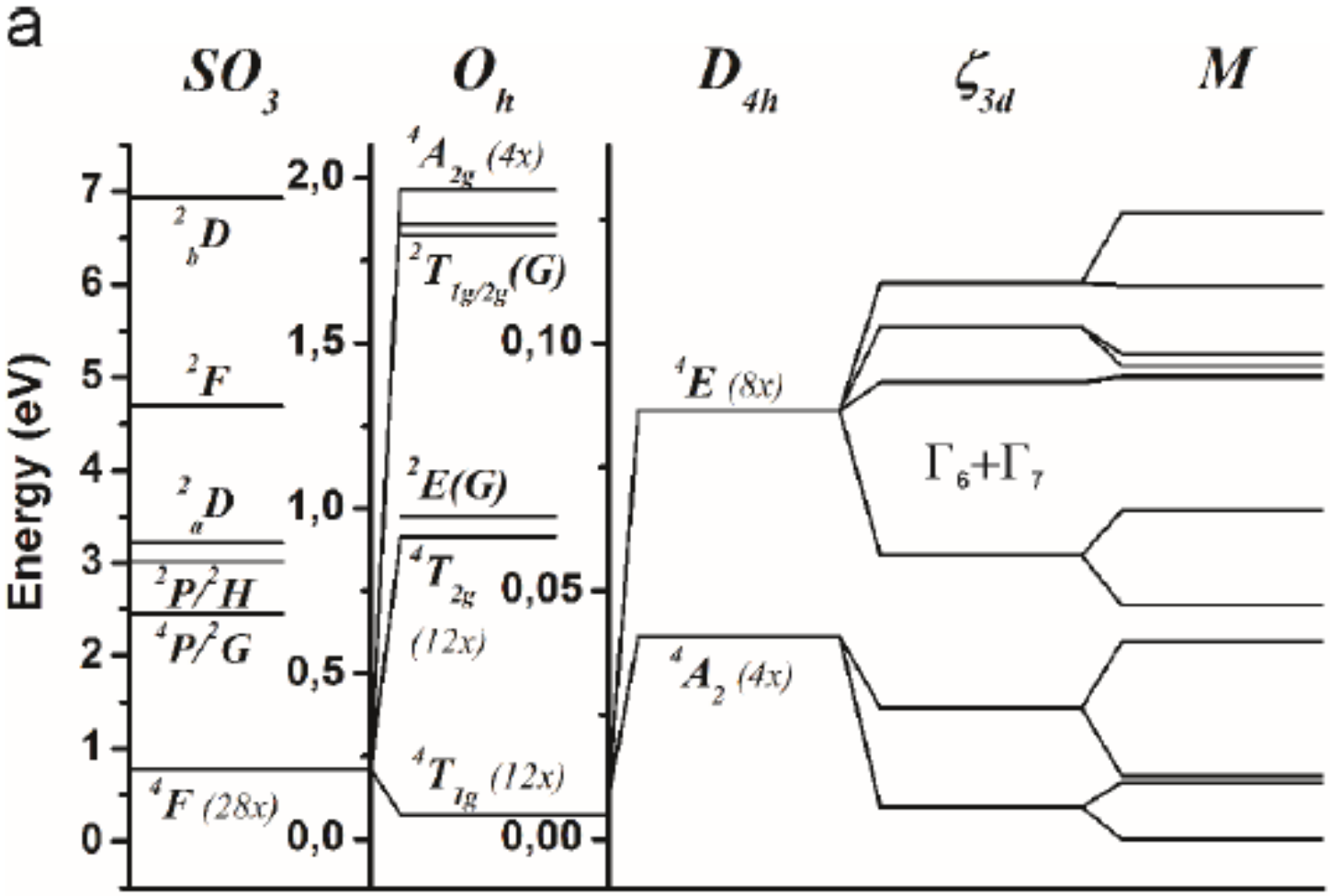
a
SO3
Oh
D4h
ζ3d
M
Energy (eV)
7
6
5
4
3
2
1
0
2,0
1,5
1,0
0,5
0,0
0,10
0,05
0,00
2Dh
2F
2Da
2P/2H
4P/2G
4F (28x)
4A2g (4x)
2T1g/2g(G)
2E(G)
4T2g
(12x)
4T1g (12x)
4E (8x)
4A2 (4x)
Γ6+Γ7