



UNIVERSITÀ
DEGLI STUDI
DI PADOVA

Chimica Inorganica 3

Lanthanoids Lectures 02



What are the difficulties with *f* electron systems?

- i) They involve *f* orbitals and these are unfamiliar;
- ii) The spin - orbit coupling is important;
- iii) The crystal and ligand field effects are small, something which poses problems when one is more familiar with complexes in which they are large.
- iv) The coordination number and geometry are much more varied (and more uncertain) than for *d* electron systems.

Fortunately, the last two problems tend to cancel each other out. When crystal field effects are small, knowledge of the detailed ligand arrangement becomes less important.

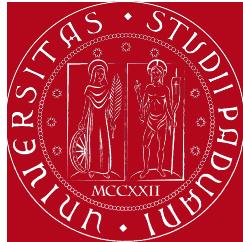


Apart from oxidation-reduction behavior, the chemistry of the earlier lanthanides resembles that of calcium(II):

- i) the oxides absorb water to give hydroxides and they absorb carbon dioxide to give carbonates.
- i) The hydroxides tend to be slightly soluble in water giving alkaline solutions, the carbonates tend to be insoluble and so on (**bastnaesite** is a Ln fluorocarbonate $M^{III}CO_3F$).

The chemistries of the later lanthanides tend to be more like that of Al, although the hydroxides are not amphoteric.

These similarities with the properties of more common ions is not just an *aide-mémoire*; it can be exploited.



Ca(II) ions are biologically very important - their movement is involved in nerve action, for example. The study of Ca(II) ions is very difficult because they lack any convenient spectroscopic property - a spectroscopic "handle" - by which they can be studied.

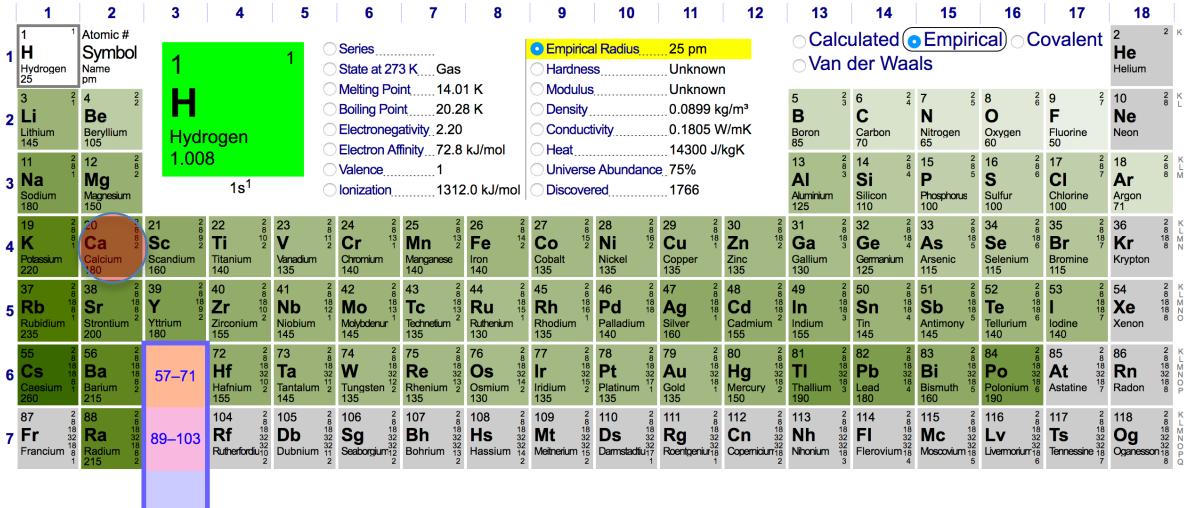
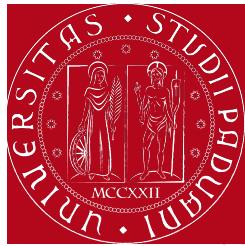
Because of their similar chemistries, it is possible to replace Ca(II) with an ion such as Tb(III), which does have convenient handles. Study of Tb(III) then gives the information we could not get directly for Ca(II). Such replacements are a popular trick in bioinorganic chemistry.

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Ca(II)	6-coordinate, oct.	114 pm
Ca(II)	8-coordinate	126 pm
Tb(III)	6-coordinate, oct.	106 pm
Tb(III)	8-coordinate	118 pm



- Size decreases across row (“lanthanide contraction”)
- Most common ion is 3+, may also be 2+ or 4+



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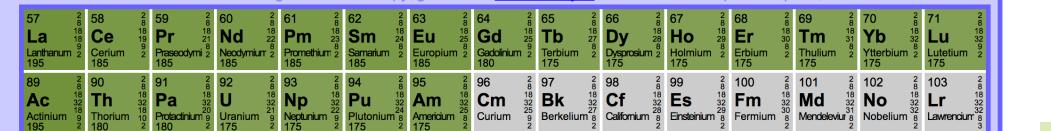


Table 1.1 The electronic configurations of lanthanide elements.

Z	Element	Electronic configurations of neutral atoms					Electronic configurations of trivalent ions	Atomic radius (pm) (coordination number = 12)	Atomic weight	
		4f	5s	5p	5d	6s				
57	La	The inner	0	2	6	1	2	[Xe]4f ⁰	187.91	138.91
58	Ce	orbitals	1	2	6	1	2	[Xe]4f ¹	182.47	140.12
59	Pr	have been	3	2	6	2		[Xe]4f ²	182.80	140.91
60	Nd	full-filled, 46	4	2	6	2		[Xe]4f ³	182.14	144.24
61	Pm	electrons	5	2	6	2		[Xe]4f ⁴	(181.0)	(147)
62	Sm	in all	6	2	6	2		[Xe]4f ⁵	180.41	150.36
63	Eu		7	2	6	2		[Xe]4f ⁶	204.20	151.96
64	Gd		7	2	6	1	2	[Xe]4f ⁷	180.13	157.25
65	Tb		9	2	6	2		[Xe]4f ⁸	178.33	158.93
66	Dy		10	2	6	2		[Xe]4f ⁹	177.40	162.50
67	Ho		11	2	6	2		[Xe]4f ¹⁰	176.61	164.93
68	Er		12	2	6	2		[Xe]4f ¹¹	175.66	167.26
69	Tm		13	2	6	2		[Xe]4f ¹²	174.62	168.93
70	Yb		14	2	6	2		[Xe]4f ¹³	193.92	173.04
71	Lu		14	2	6	1	2	[Xe]4f ¹⁴	173.49	174.97
21	Sc	Inner 18 electrons	1	2						
39	Y		10	2	6	1	2	[Kr]	180.12	88.906

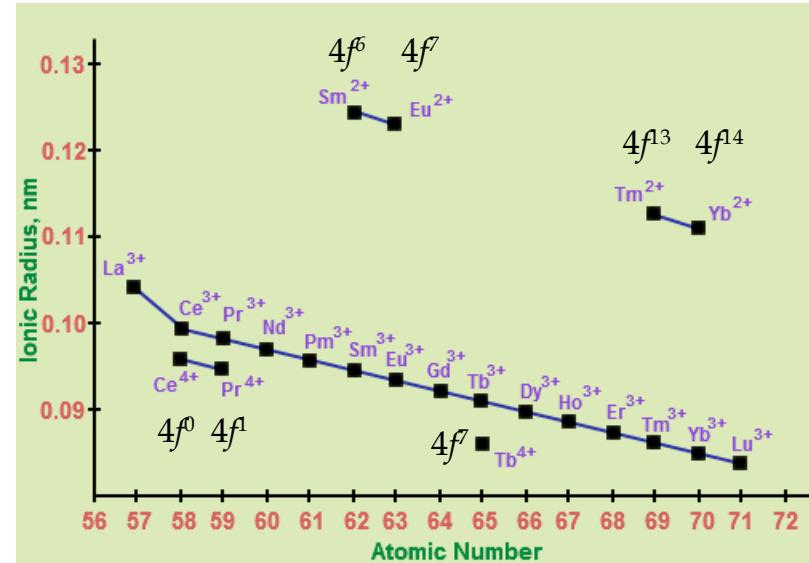
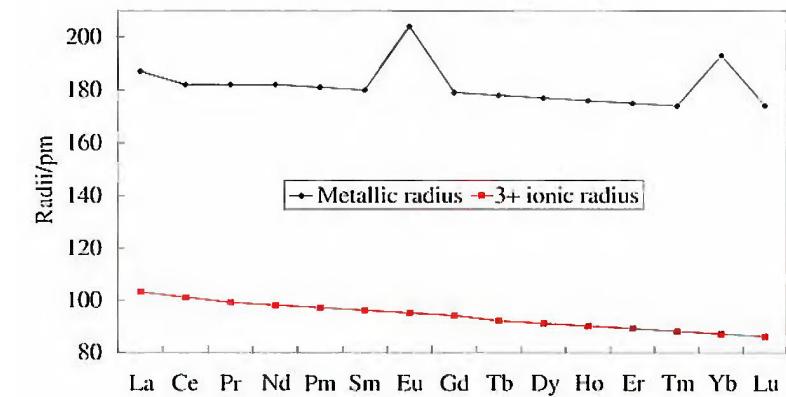
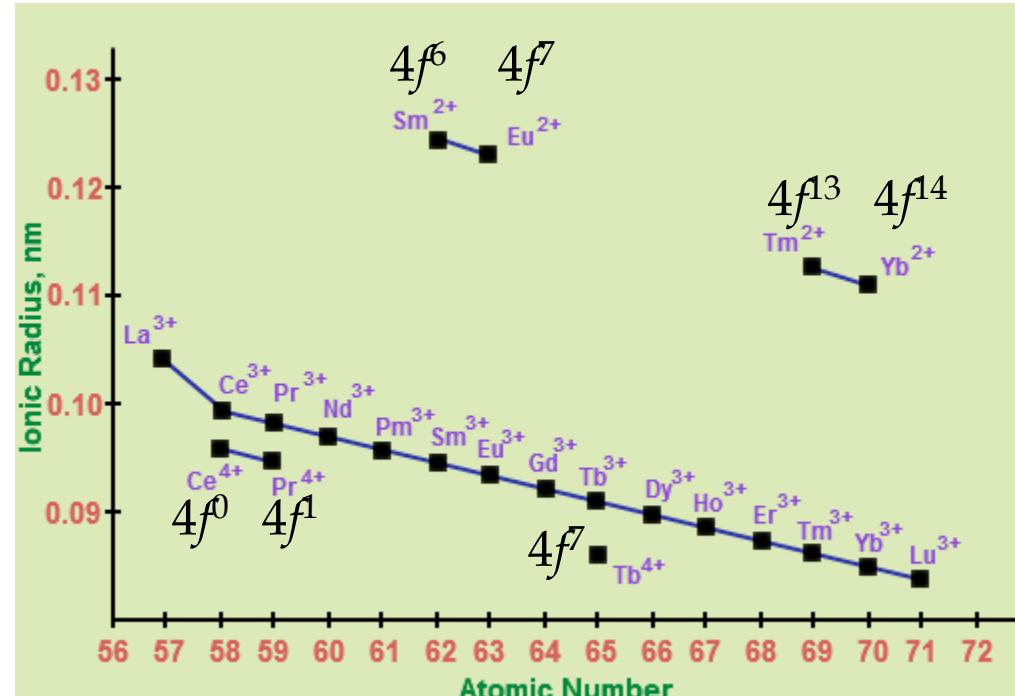


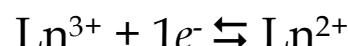


Table 1.1 The electronic configurations of lanthanide elements.

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		4f	5s	5p	5d			
57	La	The inner orbitals	0	2	6	1	2	[Xe]4f ⁰ 187.91 138.91
58	Ce	orbitals	1	2	6	1	2	[Xe]4f ¹ 182.47 140.12
59	Pr	have been full-filled, 46 electrons	3	2	6	2	[Xe]4f ² 182.80 140.91	
60	Nd		4	2	6	2	[Xe]4f ³ 182.14 144.24	
61	Pm		5	2	6	2	[Xe]4f ⁴ (181.0) (147)	
62	Sm	in all	6	2	6	2	[Xe]4f ⁵ 180.41 150.36	
63	Eu		7	2	6	2	[Xe]4f ⁶ 204.20 151.96	
64	Gd		7	2	6	1	2	[Xe]4f ⁷ 180.13 157.25
65	Tb		9	2	6	2	[Xe]4f ⁸ 178.33 158.93	
66	Dy		10	2	6	2	[Xe]4f ⁹ 177.40 162.50	
67	Ho		11	2	6	2	[Xe]4f ¹⁰ 176.61 164.93	
68	Er		12	2	6	2	[Xe]4f ¹¹ 175.66 167.26	
69	Tm		13	2	6	2	[Xe]4f ¹² 174.62 168.93	
70	Yb		14	2	6	2	[Xe]4f ¹³ 193.92 173.04	
71	Lu		14	2	6	1	2	[Xe]4f ¹⁴ 173.49 174.97
		3d	4s	4p	4d	5s		
21	Sc	Inner 18 electrons	1	2				164.06 44.956
39	Y		10	2	6	1	2	[Ar] 180.12 88.906



For many years, the lanthanides did not generate much interest, as it was believed that their chemistry was limited, owing to the restricted availability of oxidation states other than that of Ln^{3+} . Eu^{2+} , Yb^{2+} , Sm^{2+} , and Ce^{4+} were the only non-trivalent Ln ions thought achievable in molecular complexes. The reduction potentials for the process



make it clear why Ln^{2+} ions are commonly seen only for a few lanthanides: the majority of the Ln^{3+} ions have reduction potentials of -2.3 V or greater (in absolute value)

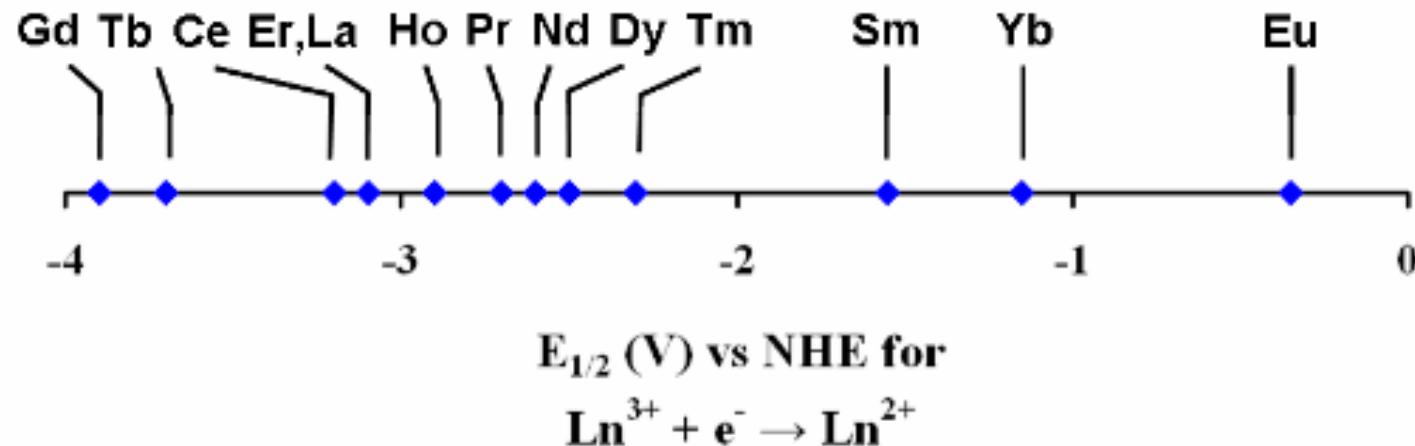


Figure 1. Reduction potentials for the $\text{Ln}^{3+} + \text{e}^- \rightarrow \text{Ln}^{2+}$ process.

Table 2.7 Redox potentials of the lanthanide ions (v)^a

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$\text{Ln}^{3+} + 3\text{e}^- \rightarrow \text{Ln}$	-2.37	-2.34	-2.35	-2.32	-2.29	-2.30	-1.99	-2.29	-2.30	-2.29	-2.33	-2.31	-2.31	-2.22	-2.30	-2.37
$\text{Ln}^{3+} + \text{e}^- \rightarrow \text{Ln}^{2+}$	(-3.1)	(-3.2)	(-2.7)	-2.6 ^b	(-2.6)	-1.55	-0.34	(-3.9)	(-3.7)	-2.5 ^b	(-2.9)	(-3.1)	-2.3 ^b	-1.05		
$\text{Ln}^{4+} + \text{e}^- \rightarrow \text{Ln}^{3+}$	1.70	(3.4)	(4.6)	(4.9)	(5.2)	(6.4)	(7.9)	(3.3)	(5.0)	(6.2)	(6.1)	(6.1)	(7.1)	(8.5)		

^a Values in parentheses are estimated.

^b = in THF.

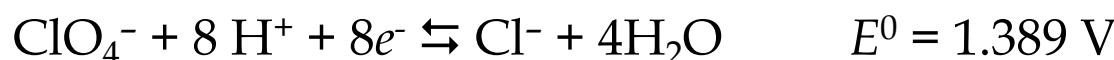




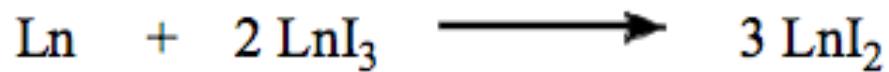
Table 2.7 Redox potentials of the lanthanide ions (v)^a

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$\text{Ln}^{3+} + 3e \rightarrow \text{Ln}^{2+}$	-2.37	-2.34	-2.35	-2.32	-2.29	-2.30	-1.99	-2.29	-2.30	-2.29	-2.33	-2.31	-2.31	-2.22	-2.30	-2.37
$\text{Ln}^{3+} + e \rightarrow \text{Ln}^{2+}$	(-3.1)	(-3.2)	(-2.7)	-2.6 ^b	(-2.6)	-1.55	-0.34	(-3.9)	(-3.7)	-2.5 ^b	(-2.9)	(-3.1)	-2.3 ^b	-1.05		
$\text{Ln}^{4+} + e \rightarrow \text{Ln}^{3+}$		1.70	(3.4)	(4.6)	(4.9)	(5.2)	(6.4)	(7.9)	(3.3)	(5.0)	(6.2)	(6.1)	(6.1)	(7.1)	(8.5)	

^a Values in parentheses are estimated.

^b = in THF.

Synproportionation



Synthesis from Pure Elements



Reduction of Ln^{3+}

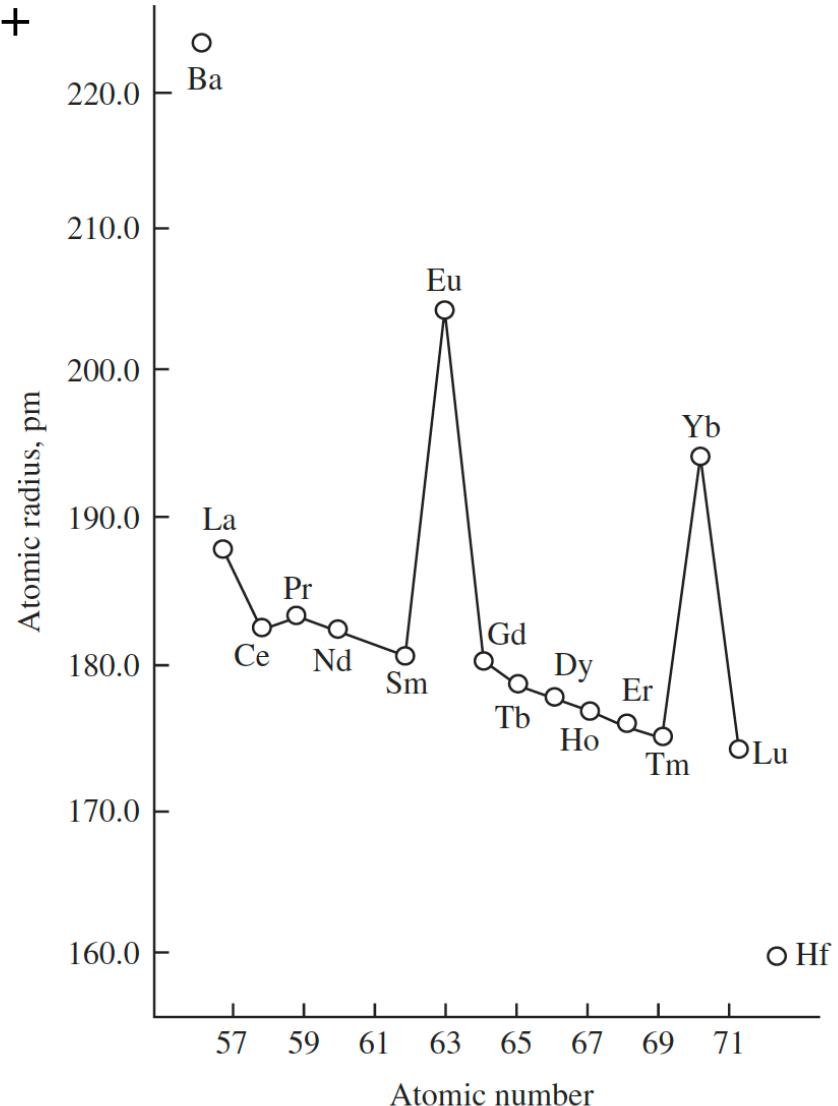
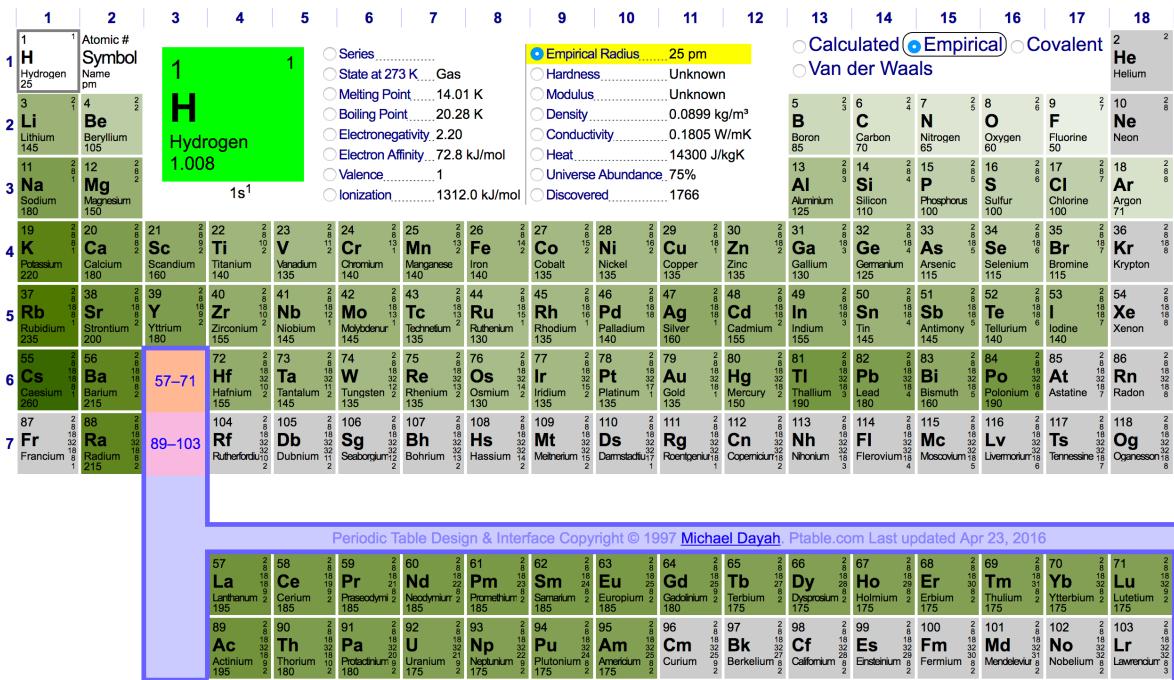


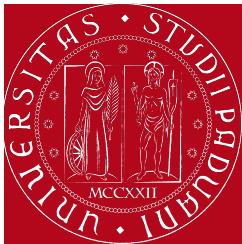
$$n = 2, 3 \quad m = 0, 1$$

Scheme 1. Synthetic methods for obtaining divalent lanthanides other than Sm^{2+} , Eu^{2+} , and Yb^{2+} .



- Size decreases across row (“lanthanide contraction”)
- Most common ion is 3+, may also be 2+ or 4+





$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} 2$$

$$R_{20}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{2\sqrt{2}} (2 - \rho_n)$$

$$R_{21}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{2\sqrt{6}} \rho_n$$

$$R_{30}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{9\sqrt{3}} (6 - 6\rho_n + \rho_n^2)$$

$$R_{31}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{9\sqrt{6}} (4 - \rho_n) \rho_n$$

$$R_{32}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{9\sqrt{30}} \rho_n^2$$

$$R_{40}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{96} (24 - 36\rho_n + 12\rho_n^2 - \rho_n^3)$$

$$R_{41}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{32\sqrt{15}} (20 - 10\rho_n + \rho_n^2) \rho_n$$

$$R_{42}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{96\sqrt{5}} (6 - \rho_n) \rho_n^2$$

$$R_{43}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{96\sqrt{35}} \rho_n^3$$

$$R_{50}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{300\sqrt{5}} (120 - 240\rho_n + 120\rho_n^2 - 20$$

$$R_{51}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{150\sqrt{30}} (120 - 90\rho_n + 18\rho_n^2 - \rho_n^3)$$

$$R_{52}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{150\sqrt{70}} (42 - 14\rho_n + \rho_n^2) \rho_n^2$$

$$R_{53}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{300\sqrt{70}} (8 - \rho_n) \rho_n^3$$

$$R_{54}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{900\sqrt{70}} \rho_n^4$$

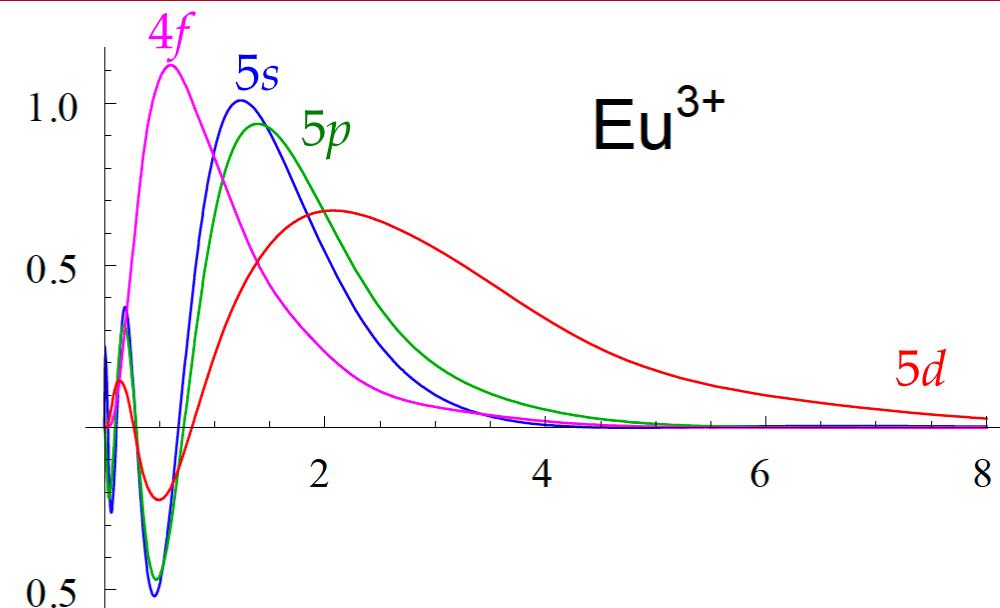
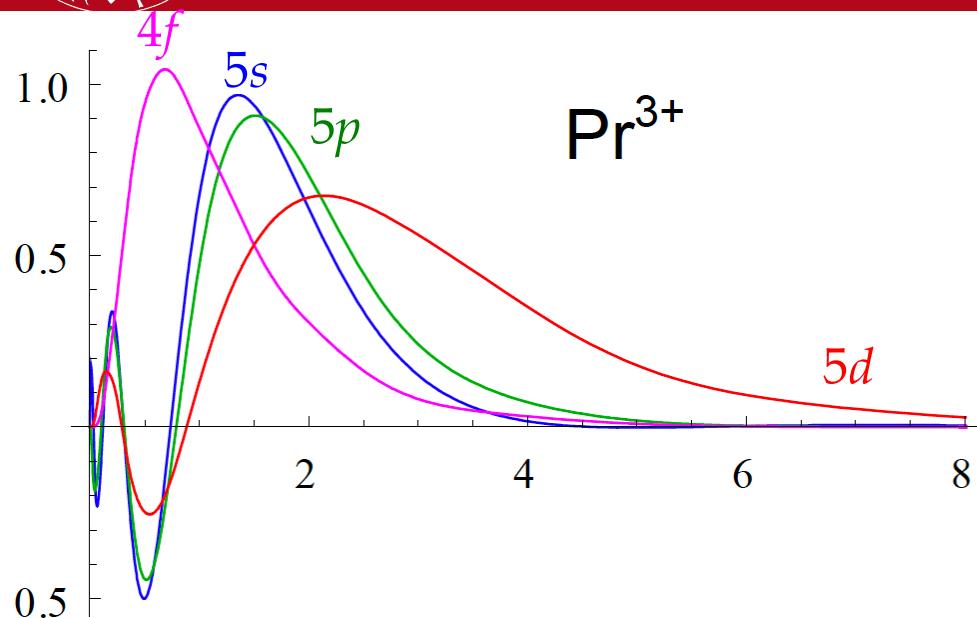
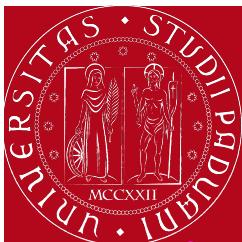
$$\rho_n \equiv \frac{2Z}{a_0 n}$$



No radial nodes

$$\begin{aligned} R_{10}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} 2 \\ R_{20}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{2\sqrt{2}} (2 - \rho_n) \\ R_{21}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{2\sqrt{6}} \rho_n \\ R_{30}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{9\sqrt{3}} (6 - 6\rho_n + \rho_n^2) \\ R_{31}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{9\sqrt{6}} (4 - \rho_n) \rho_n \\ R_{32}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{9\sqrt{30}} \rho_n^2 \\ R_{40}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{96} (24 - 36\rho_n + 12\rho_n^2 - \rho_n^3) \\ R_{41}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{32\sqrt{15}} (20 - 10\rho_n + \rho_n^2) \rho_n \\ R_{42}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{96\sqrt{5}} (6 - \rho_n) \rho_n^2 \\ R_{43}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{96\sqrt{35}} \rho_n^3 \\ R_{50}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{300\sqrt{5}} (120 - 240\rho_n + 120\rho_n^2 - 20\rho_n^3) \\ R_{51}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{150\sqrt{30}} (120 - 90\rho_n + 18\rho_n^2 - \rho_n^3) \\ R_{52}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{150\sqrt{70}} (42 - 14\rho_n + \rho_n^2) \rho_n^2 \\ R_{53}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{300\sqrt{70}} (8 - \rho_n) \rho_n^3 \\ R_{54}(r) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{900\sqrt{70}} \rho_n^4 \end{aligned}$$

$$\rho_n \equiv \frac{2Z}{a_0 n} r$$



Plots of the radial functions $rR(r)$ vs r (in a.u.) for $\text{Pr}(\text{III})$ and $\text{Eu}(\text{III})$. Pink, blue, green and red lines correspond to $4f$, $5s$, $5p$ and $5d$.

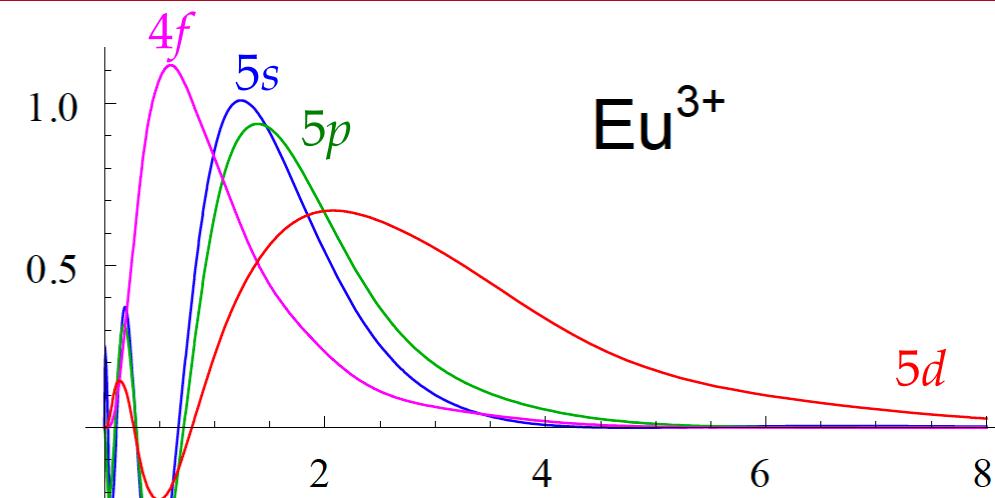
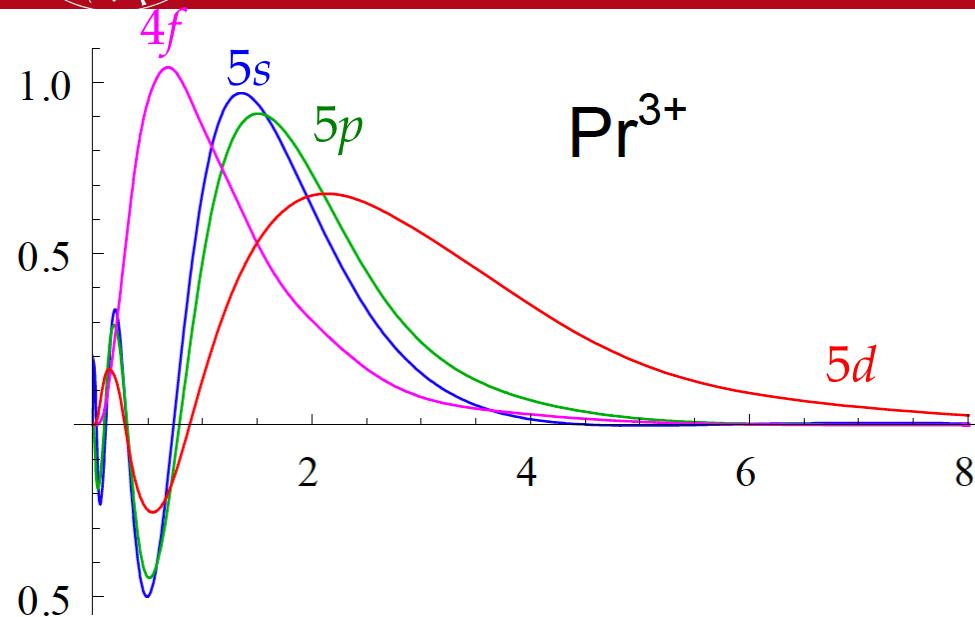
$$R_{50}(r) = \frac{1}{300\sqrt{5}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_5}{2}} (120 - 240\rho_5 + 120\rho_5^2 - 20\rho_5^3 + \rho_5^4)$$

$$R_{51}(r) = \frac{1}{150\sqrt{30}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_5}{2}} (120 - 90\rho_5 + 18\rho_5^2 - \rho_5^3) \rho_5$$

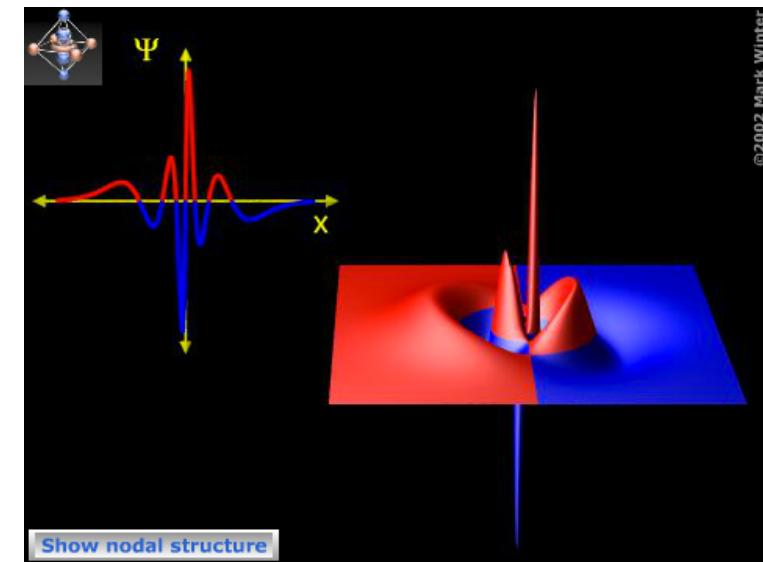
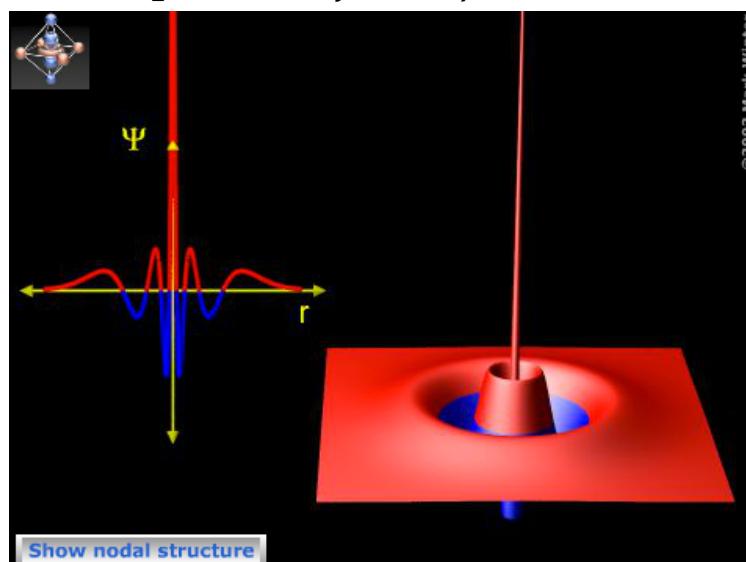
$$R_{52}(r) = \frac{1}{150\sqrt{70}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_5}{2}} (42 - 14\rho_5 + \rho_5^2) \rho_5^2$$

$$R_{43}(r) = \frac{1}{96\sqrt{35}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_4}{2}} \rho_4^3$$

$$\rho_n \equiv \frac{2Z}{a_0 n} r$$



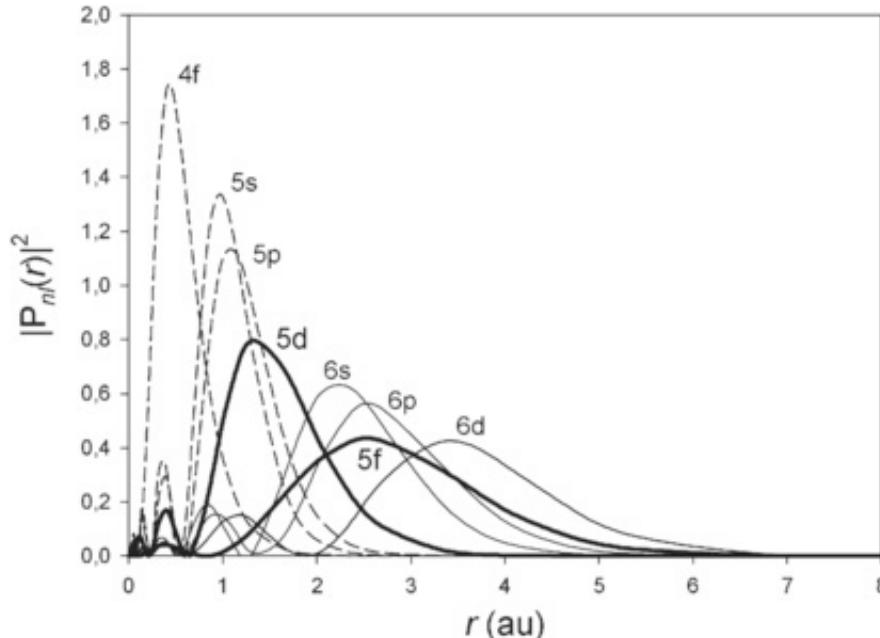
Plots of the radial functions $rR(r)$ vs r (in a.u.) for $\text{Pr}(\text{III})$ and $\text{Eu}(\text{III})$. Pink, blue, green and red lines correspond to $4f$, $5s$, $5p$ and $5d$.





Chimica Inorganica 3

Size decreases across row (“lanthanide contraction”)



Radial probability functions for hydrogen-like orbitals. Although the $4f$ AOs have their maximum closer to the nucleus than $5d$ and $6s$, close to the nucleus the density of the latter two both exceed that of the $4f$.

Periodic Table of the Elements																																																																												
Atomic Properties of the Elements																																																																												
Physical Measurement Laboratory																																																																												
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1	1 $^1S_{\frac{1}{2}}$ H Hydrogen 1.008 1s 13.9894	2	13 $^3P_{\frac{1}{2}}$ Boron 10.81 1s ² 2s ²		14 $^3P_{\frac{1}{2}}$ Carbon 12.011 1s ² 2s ²		15 $^3P_{\frac{1}{2}}$ Nitrogen 14.007 ¹ 1s ² 2s ²		16 $^3P_{\frac{1}{2}}$ Oxygen 15.999 ¹ 1s ² 2s ²		17 $^3P_{\frac{1}{2}}$ Fluorine 18.99840316 1s ² 2p ⁵		10 $^3S_{\frac{1}{2}}$ Neon 20.1797 1s ² 2p ⁶		2 $^1S_{\frac{1}{2}}$ He Helium 4.002602 1s ²																																																													
1		Frequently used fundamental physical constants For the most accurate values of these and other constants, visit physics.nist.gov/constants 1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs																																																																										
2	3 $^1S_{\frac{1}{2}}$ Li Lithium 6.94 ¹ 1s ² 2s ¹	4 $^1S_{\frac{1}{2}}$ Be Boronium 9.0121831 1s ² 2s ²	speed of light in vacuum c 299 792 458 m s ⁻¹ (exact)		6.626 07 $\times 10^{-34}$ J s ($h = h/2\pi$)		9.144 26 $\times 10^{-31}$ C ($e = e/2\pi$)		9.015 099 MeV $m_e c^2$		1.672 622 $\times 10^{-10}$ kg proton mass m_p		1.197 38 $\times 10^{-10}$ kg fine-structure constant α		117 035 999 R_{∞}		10 973 731 569 eV $R_{\infty} c$																																																											
	11 $^1S_{\frac{1}{2}}$ Na Sodium 22.989 769 792 1s ² 2p ⁶	12 $^1S_{\frac{1}{2}}$ Mg Magnesium 24.369 1s ² 2p ⁶	Rydberg constant R_{∞}		1.380 569 eV Boltzmann constant k		3.289 841 960 $\times 10^{-10}$ Hz $R_{\infty} c$		1.380 6 $\times 10^{-10}$ J K ⁻¹ k		Physical Measurement Laboratory www.nist.gov/pml		Standard Reference Data www.nist.gov/srd		18 VIIIa																																																													
3	3 $^1S_{\frac{1}{2}}$ Sc Scandium 44.95908 1s ² 2p ⁶	4 $^{1D}_{\frac{5}{2}}$ Ti Titanium 45.9878 1s ² 2p ⁶	13 $^3P_{\frac{1}{2}}$ Aluminum 26.9851395 1s ² 2p ⁶		14 $^3P_{\frac{1}{2}}$ Silicon 28.085 1s ² 2p ⁶		15 $^3P_{\frac{1}{2}}$ Phosphorus 30.973 421 965 1s ² 2p ⁶		16 $^3P_{\frac{1}{2}}$ Chlorine 35.945 1s ² 2p ⁶		17 $^3P_{\frac{1}{2}}$ Ar Argon 39.946 1s ² 2p ⁶		18 VIIIa		18 VIIIa																																																													
	5 $^{1D}_{\frac{5}{2}}$ Ca Calcium 40.078 1s ² 2p ⁶	6 $^{1D}_{\frac{5}{2}}$ V Vanadium 45.95908 1s ² 2p ⁶	19 $^1S_{\frac{1}{2}}$ K Potassium 39.093 1s ² 2p ⁶		20 $^{1D}_{\frac{5}{2}}$ Sc Scandium 44.95908 1s ² 2p ⁶		21 $^{1D}_{\frac{5}{2}}$ Ti Titanium 45.9878 1s ² 2p ⁶		22 $^{1D}_{\frac{5}{2}}$ V Vanadium 45.95908 1s ² 2p ⁶		23 $^{1D}_{\frac{5}{2}}$ Cr Chromium 55.981 1s ² 2p ⁶		24 $^{1D}_{\frac{5}{2}}$ Mn Manganese 56.9415 1s ² 2p ⁶		25 $^{1D}_{\frac{5}{2}}$ Fe Iron 55.98044 1s ² 2p ⁶		26 $^{1D}_{\frac{5}{2}}$ Co Cobalt 55.98194 1s ² 2p ⁶		27 $^{1D}_{\frac{5}{2}}$ Ni Nickel 55.98214 1s ² 2p ⁶		28 $^{1D}_{\frac{5}{2}}$ Cu Copper 58.933194 1s ² 2p ⁶		29 $^{1D}_{\frac{5}{2}}$ Zn Zinc 63.554 1s ² 2p ⁶		30 $^{1D}_{\frac{5}{2}}$ Ge Germanium 65.528 1s ² 2p ⁶		31 $^{1D}_{\frac{5}{2}}$ As Arsenic 76.971 1s ² 2p ⁶		32 $^{1D}_{\frac{5}{2}}$ Se Selenium 78.993 1s ² 2p ⁶		33 $^{1D}_{\frac{5}{2}}$ Te Tellurium 126.90407 1s ² 2p ⁶		34 $^{1D}_{\frac{5}{2}}$ Kr Krypton 131.933 1s ² 2p ⁶																																											
4	19 $^{1D}_{\frac{5}{2}}$ K Potassium 39.093 1s ² 2p ⁶	20 $^{1D}_{\frac{5}{2}}$ Ca Calcium 40.078 1s ² 2p ⁶	35 $^{1D}_{\frac{5}{2}}$ Rb Rubidium 85.6678 1s ² 2p ⁶		36 $^{1D}_{\frac{5}{2}}$ Sr Strontium 88.95884 1s ² 2p ⁶		37 $^{1D}_{\frac{5}{2}}$ Y Yttrium 89.90764 1s ² 2p ⁶		38 $^{1D}_{\frac{5}{2}}$ Zr Zirconium 91.224 1s ² 2p ⁶		39 $^{1D}_{\frac{5}{2}}$ Nb Niobium 92.9637 1s ² 2p ⁶		40 $^{1D}_{\frac{5}{2}}$ Mo Molybdenum 95.95 1s ² 2p ⁶		41 $^{1D}_{\frac{5}{2}}$ Tc Technetium 95.95 1s ² 2p ⁶		42 $^{1D}_{\frac{5}{2}}$ Ru Ruthenium 101.07 1s ² 2p ⁶		43 $^{1D}_{\frac{5}{2}}$ Rh Rhodium 106.42 1s ² 2p ⁶		44 $^{1D}_{\frac{5}{2}}$ Pd Palladium 107.8682 1s ² 2p ⁶		45 $^{1D}_{\frac{5}{2}}$ Ag Silver 109.64 1s ² 2p ⁶		46 $^{1D}_{\frac{5}{2}}$ Sb Antimony 112.414 1s ² 2p ⁶		47 $^{1D}_{\frac{5}{2}}$ Cs Cesium 130.95458 1s ² 2p ⁶		48 $^{1D}_{\frac{5}{2}}$ Ba Barium 137.327 1s ² 2p ⁶		49 $^{1D}_{\frac{5}{2}}$ Hf Hafnium 178.49 1s ² 2p ⁶		50 $^{1D}_{\frac{5}{2}}$ Ta Tantalum 181.978 1s ² 2p ⁶		51 $^{1D}_{\frac{5}{2}}$ W Tungsten 183.833 1s ² 2p ⁶		52 $^{1D}_{\frac{5}{2}}$ Re Rhenium 191.964 1s ² 2p ⁶		53 $^{1D}_{\frac{5}{2}}$ Os Osmium 196.966 1s ² 2p ⁶		54 $^{1D}_{\frac{5}{2}}$ Ir Iridium 199.966 1s ² 2p ⁶		55 $^{1D}_{\frac{5}{2}}$ Pt Platinum 208.593 1s ² 2p ⁶		56 $^{1D}_{\frac{5}{2}}$ Au Gold 208.9940 1s ² 2p ⁶		57 $^{1D}_{\frac{5}{2}}$ Hg Mercury 209.509 1s ² 2p ⁶		58 $^{1D}_{\frac{5}{2}}$ Tl Thallium 204.388 1s ² 2p ⁶		59 $^{1D}_{\frac{5}{2}}$ Pb Lead 208.9840 1s ² 2p ⁶		60 $^{1D}_{\frac{5}{2}}$ Bi Bismuth (209) 1s ² 2p ⁶		61 $^{1D}_{\frac{5}{2}}$ Po Polonium (210) 1s ² 2p ⁶		62 $^{1D}_{\frac{5}{2}}$ At Astatine (211) 1s ² 2p ⁶		63 $^{1D}_{\frac{5}{2}}$ Rn Radium (222) 1s ² 2p ⁶		64 $^{1D}_{\frac{5}{2}}$ Rb Rubidium (226) 1s ² 2p ⁶		65 $^{1D}_{\frac{5}{2}}$ Sr Strontium (228) 1s ² 2p ⁶		66 $^{1D}_{\frac{5}{2}}$ Cs Cesium (229) 1s ² 2p ⁶		67 $^{1D}_{\frac{5}{2}}$ Ba Barium (231) 1s ² 2p ⁶		68 $^{1D}_{\frac{5}{2}}$ La Lanthanum (232) 1s ² 2p ⁶		69 $^{1D}_{\frac{5}{2}}$ Ce Cerium (238) 1s ² 2p ⁶		70 $^{1D}_{\frac{5}{2}}$ Yb Ytterbium (173) 1s ² 2p ⁶		71 $^{1D}_{\frac{5}{2}}$ Lu Lutetium (175) 1s ² 2p ⁶	
6	55 $^{1D}_{\frac{5}{2}}$ Cs Cesium 130.95458 1s ² 2p ⁶	56 $^{1S}_{\frac{1}{2}}$ Sr Strontium 88.95884 1s ² 2p ⁶	72 $^{1D}_{\frac{5}{2}}$ Ba Barium 137.327 1s ² 2p ⁶		73 $^{1D}_{\frac{5}{2}}$ Hf Hafnium 178.49 1s ² 2p ⁶		74 $^{1D}_{\frac{5}{2}}$ Tc Tantalum 181.978 1s ² 2p ⁶		75 $^{1D}_{\frac{5}{2}}$ Os Osmium 191.964 1s ² 2p ⁶		76 $^{1D}_{\frac{5}{2}}$ Ir Iridium 196.966 1s ² 2p ⁶		77 $^{1D}_{\frac{5}{2}}$ Pt Platinum 208.593 1s ² 2p ⁶		78 $^{1D}_{\frac{5}{2}}$ Au Gold 208.9940 1s ² 2p ⁶		79 $^{1D}_{\frac{5}{2}}$ Hg Mercury 209.509 1s ² 2p ⁶		80 $^{1D}_{\frac{5}{2}}$ Tl Thallium 204.388 1s ² 2p ⁶		81 $^{1D}_{\frac{5}{2}}$ Pb Lead (207) 1s ² 2p ⁶		82 $^{1D}_{\frac{5}{2}}$ Bi Bismuth (209) 1s ² 2p ⁶		83 $^{1D}_{\frac{5}{2}}$ Po Polonium (210) 1s ² 2p ⁶		84 $^{1D}_{\frac{5}{2}}$ At Astatine (211) 1s ² 2p ⁶		85 $^{1D}_{\frac{5}{2}}$ Rn Radium (222) 1s ² 2p ⁶		86 $^{1S}_{\frac{1}{2}}$ Rn Radium (226) 1s ² 2p ⁶																																													
	55 $^{1D}_{\frac{5}{2}}$ Cs Cesium 130.95458 1s ² 2p ⁶	56 $^{1S}_{\frac{1}{2}}$ Sr Strontium 88.95884 1s ² 2p ⁶	87 $^{1D}_{\frac{5}{2}}$ Fr Francium (223) 1s ² 2p ⁶		88 $^{1D}_{\frac{5}{2}}$ Rf Rutherfordium (261) 1s ² 2p ⁶		89 $^{1D}_{\frac{5}{2}}$ Ac Actinium (227) 1s ² 2p ⁶		90 $^{1D}_{\frac{5}{2}}$ Th Thorium (232) 1s ² 2p ⁶		91 $^{1D}_{\frac{5}{2}}$ Pa Protactinium (231) 1s ² 2p ⁶		92 $^{1D}_{\frac{5}{2}}$ U Uranium (238) 1s ² 2p ⁶		93 $^{1L}_{\frac{5}{2}}$ Np Neptunium (237) 1s ² 2p ⁶		94 $^{1F}_{\frac{5}{2}}$ Pu Plutonium (244) 1s ² 2p ⁶		95 $^{1S}_{\frac{1}{2}}$ Am Americium (243) 1s ² 2p ⁶		96 $^{1D}_{\frac{5}{2}}$ Cm Curium (247) 1s ² 2p ⁶		97 $^{1F}_{\frac{5}{2}}$ Bk Berkelium (249) 1s ² 2p ⁶		98 $^{1S}_{\frac{1}{2}}$ Cf Californium (251) 1s ² 2p ⁶		99 $^{1D}_{\frac{5}{2}}$ Es Einsteinium (252) 1s ² 2p ⁶		100 $^{1H}_{\frac{1}{2}}$ Md Mendeleyevium (253) 1s ² 2p ⁶		102 $^{1S}_{\frac{1}{2}}$ No Neutronium (262) 1s ² 2p ⁶		103 $^{1P}_{\frac{1}{2}}$ Lr Lutetium (264) 1s ² 2p ⁶																																											
7	87 $^{1D}_{\frac{5}{2}}$ Fr Francium (223) 1s ² 2p ⁶	88 $^{1D}_{\frac{5}{2}}$ Ac Actinium (227) 1s ² 2p ⁶	90 $^{1D}_{\frac{5}{2}}$ Th Thorium (232) 1s ² 2p ⁶		91 $^{1D}_{\frac{5}{2}}$ Pa Protactinium (231) 1s ² 2p ⁶		92 $^{1D}_{\frac{5}{2}}$ U Uranium (238) 1s ² 2p ⁶		93 $^{1L}_{\frac{5}{2}}$ Np Neptunium (237) 1s ² 2p ⁶		94 $^{1F}_{\frac{5}{2}}$ Pu Plutonium (244) 1s ² 2p ⁶		95 $^{1S}_{\frac{1}{2}}$ Am Americium (243) 1s ² 2p ⁶		96 $^{1D}_{\frac{5}{2}}$ Cm Curium (247) 1s ² 2p ⁶		97 $^{1F}_{\frac{5}{2}}$ Bk Berkelium (249) 1s ² 2p ⁶		98 $^{1S}_{\frac{1}{2}}$ Cf Californium (251) 1s ² 2p ⁶		99 $^{1D}_{\frac{5}{2}}$ Es Einsteinium (252) 1s ² 2p ⁶		100 $^{1H}_{\frac{1}{2}}$ Md Mendeleyevium (253) 1s ² 2p ⁶		102 $^{1S}_{\frac{1}{2}}$ No Neutronium (262) 1s ² 2p ⁶		103 $^{1P}_{\frac{1}{2}}$ Lr Lutetium (264) 1s ² 2p ⁶																																																	
	55 $^{1D}_{\frac{5}{2}}$ Cs Cesium 130.95458 1s ² 2p ⁶	56 $^{1S}_{\frac{1}{2}}$ Sr Strontium 88.95884 1s ² 2p ⁶	104 $^{1D}_{\frac{5}{2}}$ Fr Rutherfordium (261) 1s ² 2p ⁶		105 $^{1D}_{\frac{5}{2}}$ Rf Rutherfordium (261) 1s ² 2p ⁶		106 $^{1S}_{\frac{1}{2}}$ Ac Actinium (227) 1s ² 2p ⁶		107 $^{1D}_{\frac{5}{2}}$ Th Thorium (238) 1s ² 2p ⁶		108 $^{1S}_{\frac{1}{2}}$ Hs Hassium (263) 1s ² 2p ⁶		109 $^{1D}_{\frac{5}{2}}$ Mt Mentenium (276) 1s ² 2p ⁶		110 $^{1D}_{\frac{5}{2}}$ Ds Darmstadtium (281) 1s ² 2p ⁶		111 $^{1D}_{\frac{5}{2}}$ Rg Roentgenium (280) 1s ² 2p ⁶		112 $^{1D}_{\frac{5}{2}}$ Cn Copernicium (285) 1s ² 2p ⁶		113 $^{1D}_{\frac{5}{2}}$ Uut Ununtrium (284) 1s ² 2p ⁶		114 $^{1F}_{\frac{5}{2}}$ Fl Flerovium (289) 1s ² 2p ⁶		115 $^{1D}_{\frac{5}{2}}$ Uup Ununpentium (288) 1s ² 2p ⁶		116 $^{1L}_{\frac{5}{2}}$ Lv Livermorium (293) 1s ² 2p ⁶		117 $^{1D}_{\frac{5}{2}}$ Lw Livermorium (294) 1s ² 2p ⁶		118 $^{1S}_{\frac{1}{2}}$ Uuo Ununquadium (294) 1s<																																													

$4f$ orbitals are highly nodal and since all the angular nodes pass through the nucleus, the probability of finding an f electron close to the nucleus is low. The $5d$ and $6s$ orbitals, which are formally empty orbitals, may well accept (paired) electrons donated by ligands and in so doing help to determine the ionic radius of the lanthanide. But electrons in these orbitals have a much higher probability of being very close to the nucleus than do $4f$.

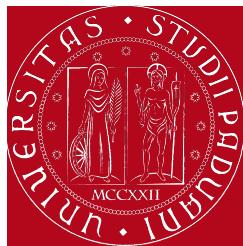


- Silvery white metals with high melting and boiling points

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18				
1 H Idrogeno 14.01	1 Simbolo Nome Kelvin	56 Ba Bario 137,327	2 8 18 18 2	○ Serie Alkaline	○ State at 273 K Solidi	○ Punto di fusione 1000 K	○ Punto di ebollizione 2143 K	○ Elettronegatività 0.89	○ Affinità elettronica 13.95 kJ/mol	○ Valenza 2	○ Energia di ionizzazione 502.9 kJ/mol	○ Radius 253 pm	○ Durezza Sconosciuto	○ Modulus 9.6 GPa	○ Densità 3510 kg/m ³	5 B Boro 2348	6 C Carbonio 3823	7 N Azoto 63.05	8 O Ossigeno 53.5	9 F Fluoro 53.5	273 ⚡
3 Li Litio 453.69	4 Be Berillio 1560	11 Na Sodio 370.87	12 Mg Magnesio 923	[Xe] 6s ²	20 Ca Calcio 1115	21 Sc Scandio 1814	22 Ti Titanio 1941	23 V Vanadio 2183	24 Cr Cromo 2180	25 Mn Manganese 1519	26 Fe Ferro 1811	27 Co Cobalto 1768	28 Ni Nichel 1728	29 Cu Rame 1357.77	30 Zn Zinco 692.68	31 Ga Gallio 302.91	32 Ge Germanio 1211.4	33 As Arsenico 1090	34 Se Selenio 494	35 Br Bromo 265.8	36 Kr Kripton 115.79
19 K Potassio 336.53	20 Ca Calcio 1115	21 Sc Scandio 1814	22 Ti Titanio 1941	23 V Vanadio 2183	24 Cr Cromo 2180	25 Mn Manganese 1519	26 Fe Ferro 1811	27 Co Cobalto 1768	28 Ni Nichel 1728	29 Cu Rame 1357.77	30 Zn Zinco 692.68	31 Ga Gallio 302.91	32 Ge Germanio 1211.4	33 As Arsenico 1090	34 Se Selenio 494	35 Br Bromo 265.8	36 Kr Kripton 115.79				
37 Rb Rubidio 312.46	38 Sr Stronzio 1050	39 Y Ittrio 1799	40 Zr Zirconio 2128	41 Nb Niobio 2750	42 Mo Molibdeno 2896	43 Tc Tecnecio 2430	44 Ru Rutenio 2607	45 Rh Rodio 2237	46 Pd Palladio 1828.05	47 Ag Argento 1234.93	48 Cd Cadmio 594.22	49 In Indio 429.75	50 Sn Stagno 505.08	51 Sb Antimonio 903.78	52 Te Tellurio 722.66	53 I Iodio 386.85	54 Xe Xeno 161.3	55 Cs Cesio 301.59			
56 Ba Bario 1000	57-71 Hf Afnio 2506	72 Ta Tantalo 3290	73 W Tungsteno 3695	74 Re Renio 3459	75 Os Osmio 3306	76 Ir Iridio 2739	77 Pt Platino 2041.4	78 Au Oro 1337.33	79 Hg Mercurio 234.32	80 Tl Tallio 577	81 Pb Piombo 600.61	82 Bi Bismuto 544.4	83 Po Polonio 527	84 At Astato 575	85 Rn Radon 202	86 At Astato 575	87 Fr Francio 300				
88 Ra Radio 1973	89-103 Rf Rutherfordio 10	104 Rf Rutherfordio 10	105 Db Dubnio 11	106 Sg Seaborgio 12	107 Bh Bohrio 13	108 Hs Hassio 14	109 Mt Meitnerio 15	110 Ds Darmstadio 17	111 Rg Roentgenio 18	112 Cn Copernicio 18	113 Nh Nihonium 18	114 Fl Flerovio 18	115 Mc Moscovium 18	116 Lv Livermorio 18	117 Ts Tennessee 18	118 Og Oganesson 18					

Darker colors indicate an element's melting point is colder (blue) or hotter (red) than the selected temperature.

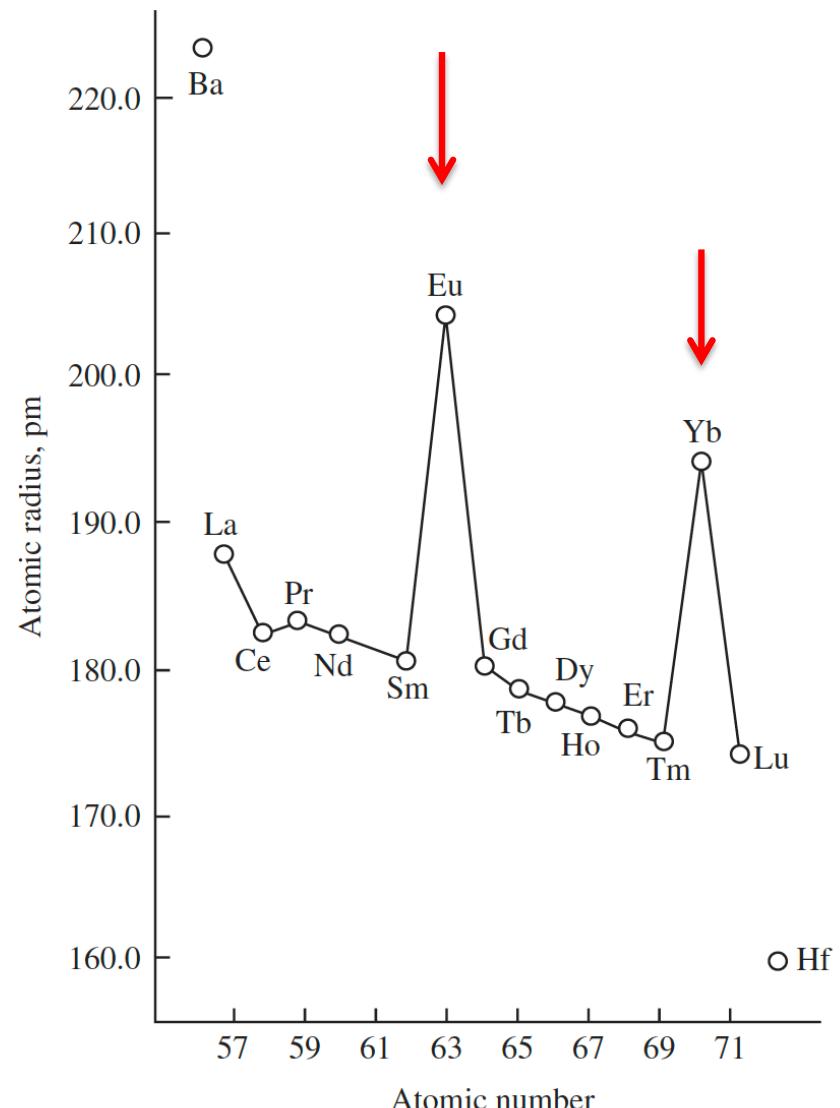
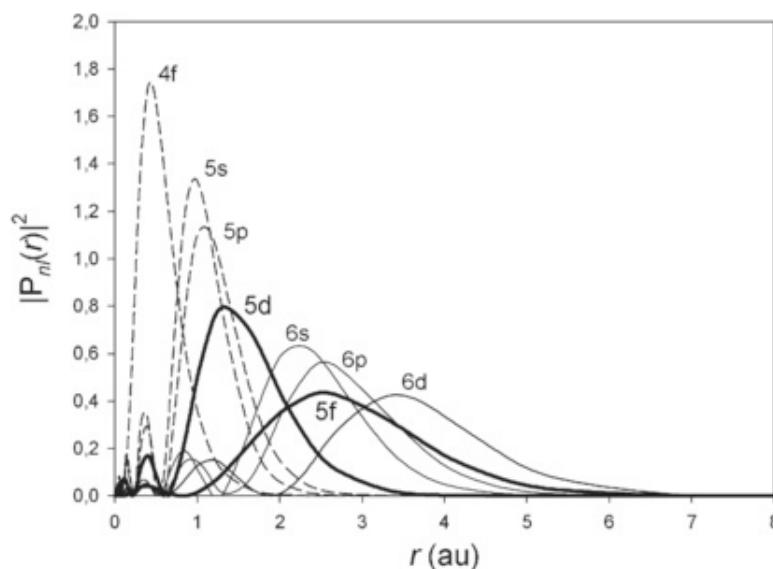
57	2	58	2	59	2	60	2	61	2	62	2	63	2	64	2	65	2	66	2	67	2	68	2	69	2	70	2	71	2
	8	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18		
La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
Lantano	2	Cerio	2	Praseodimio	2	Neodimio	2	Promezio	2	Samario	2	Europio	2	Gadolinio	2	Terbio	2	Disprosio	2	Olmio	2	Erbio	2	Tulio	2	Itterbio	2	Lutezio	2
1193		1071		1204		1294		1373		1345		1095		1586		1629		1685		1747		1770		1818		1092		1936	
89	2	90	2	91	2	92	2	93	2	94	2	95	2	96	2	97	2	98	2	99	2	100	2	101	2	102	2	103	2
	8	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18		
Ac		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr	
Attinio	9	Torio	10	Protoattinio	9	Uranio	9	Nettunio	9	Plutonio	9	Americio	8	Curio	9	Berkelio	8	Californio	8	Einsteinio	8	Mendelevio	8	Nobelio	8	Laurenzio	8	Laurenzio	8
1323	2	2023	2	1845	2	1408	2	917	2	913	2	1449	2	1618	2	1323	2	1173	2	1133	2	1800	2	1100	2	1100	2	1900	3



For lanthanide elements, as the atomic number increases an electron is not added to the outermost shell but rather to the inner 4f shell!

Table 1.1 The electronic configurations of lanthanide elements.

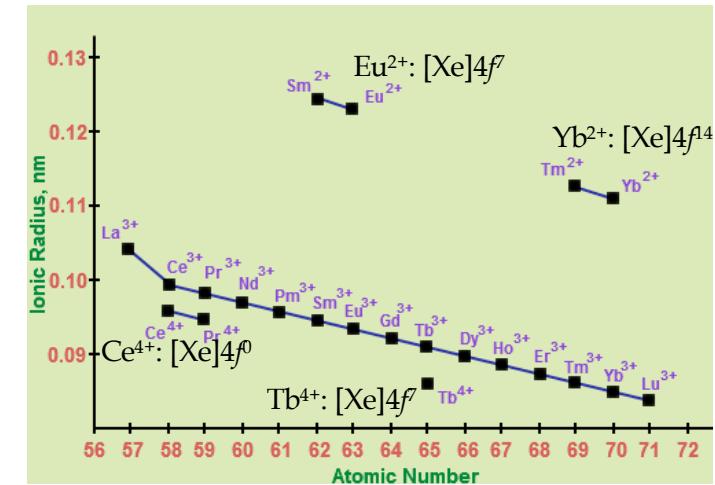
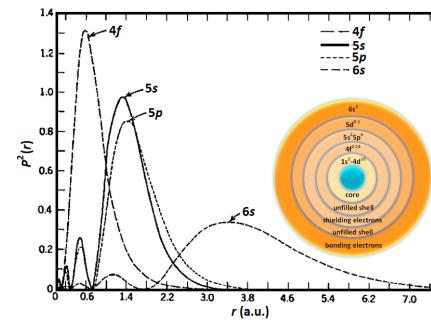
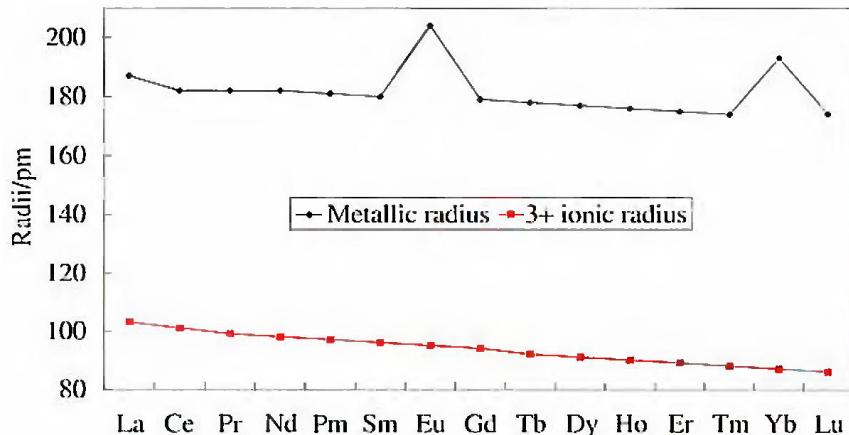
Z	Element	Electronic configurations of neutral atoms					Electronic configurations of trivalent ions	Atomic radius (pm) (coordination number = 12)	Atomic weight	
		4f	5s	5p	5d	6s				
57	La	The inner	0	2	6	1	2	[Xe]4f ⁰	187.91	138.91
58	Ce	orbitals	1	2	6	1	2	[Xe]4f ¹	182.47	140.12
59	Pr	have been	3	2	6		2	[Xe]4f ²	182.80	140.91
60	Nd	full-filled, 46	4	2	6		2	[Xe]4f ³	182.14	144.24
61	Pm	electrons	5	2	6		2	[Xe]4f ⁴	(181.0)	(147)
62	Sm	in all	6	2	6		2	[Xe]4f ⁵	180.41	150.36
63	Eu		7	2	6		2	[Xe]4f ⁶	204.20	151.96
64	Gd		7	2	6	1	2	[Xe]4f ⁷	180.13	157.25
65	Tb		9	2	6		2	[Xe]4f ⁸	178.33	158.93
66	Dy		10	2	6		2	[Xe]4f ⁹	177.40	162.50
67	Ho		11	2	6		2	[Xe]4f ¹⁰	176.61	164.93
68	Er		12	2	6		2	[Xe]4f ¹¹	175.66	167.26
69	Tm		13	2	6		2	[Xe]4f ¹²	174.62	168.93
70	Yb		14	2	6		2	[Xe]4f ¹³	193.92	173.04
71	Lu		14	2	6	1	2	[Xe]4f ¹⁴	173.49	174.97
21	Sc	Inner 18 electrons	1	2					164.06	44.956
39	Y		10	2	6	1	2	[Kr]	180.12	88.906





Chemical element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Image															
Density (g/cm ³)	6.162	6.770	6.77	7.01	7.26	7.52	5.244	7.90	8.23	8.540	8.79	9.066	9.32	6.90	9.841
Melting point (°C)	920	795	935	1024	1042	1072	826	1312	1356	1407	1461	1529	1545	824	1652
Boiling point (°C)	3464	3443	3520	3074	3000	1794	1529	3273	3230	2567	2720	2868	1950	1196	3402
Atomic electron configuration*	5d ¹	4f ¹ 5d ¹	4f ³	4f ⁴	4f ⁵	4f ⁶	4f ⁷	4f ⁷ 5d ¹	4f ⁹	4f ¹⁰	4f ¹¹	4f ¹²	4f ¹³	4f ¹⁴	4f ¹⁴ 5d ¹
Metal lattice (RT)	dhcp	fcc	dhcp	dhcp	dhcp	**	bcc	hcp	hcp	hcp	hcp	hcp	hcp	hcp	hcp
Metallic radius pm	162	181.8	182.4	181.4	183.4	180.4	208.4	180.4	177.3	178.1	176.2	176.1	175.9	193.3	173.8
Resistivity (25 °C) / μ Ohm cm	57–80 20 °C	73	68	64		88	90	134	114	57	87	87	79	29	79
mag susceptibility $\chi_{\text{mol}} / 10^{-6} (\text{cm}^3 \cdot \text{mol}^{-1})$	+95.9	+2500 (β)	+5530 (α)	+5930 (α)		+1278 (α)	+30900	+185000 (350 K)	+170000 (α)	+98000	+72900	+48000	+24700	+67 (β)	+183

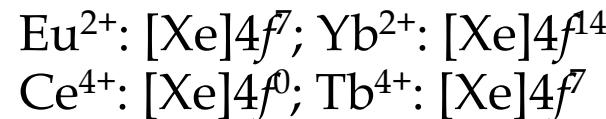
*Between initial [Xe] and final 6s² electronic shells



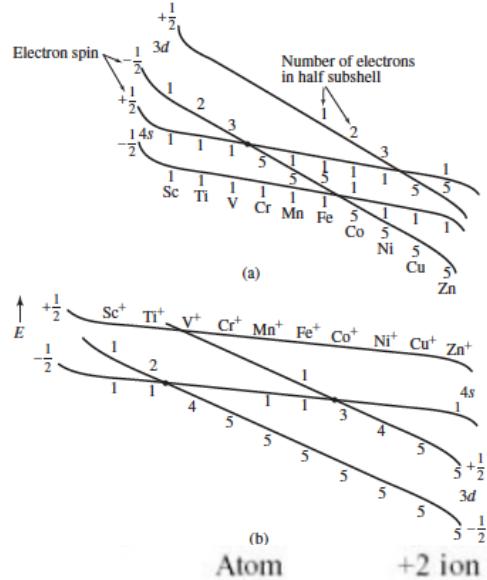
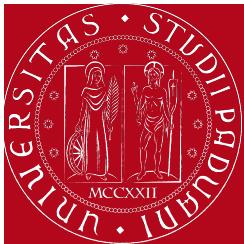


Chemical element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Image															
Density (g/cm³)	6.162	6.770	6.77	7.01	7.26	7.52	5.244	7.90	8.23	8.540	8.79	9.066	9.32	6.90	9.841
Melting point (°C)	920	795	935	1024	1042	1072	826	1312	1356	1407	1461	1529	1545	824	1652
Boiling point (°C)	3464	3443	3520	3074	3000	1794	1529	3273	3230	2567	2720	2868	1950	1196	3402
Atomic electron configuration*	5d ¹	4f ¹ 5d ¹	4f ³	4f ⁴	4f ⁵	4f ⁶	4f ⁷	4f ⁷ 5d ¹	4f ⁹	4f ¹⁰	4f ¹¹	4f ¹²	4f ¹³	4f ¹⁴	4f ¹⁴ 5d ¹
Metal lattice (RT)	dhcp	fcc	dhcp	dhcp	dhcp	**	bcc	hcp	hcp	hcp	hcp	hcp	hcp	hcp	hcp
Metallic radius pm	162	181.8	182.4	181.4	183.4	180.4	208.4	180.4	177.3	178.1	176.2	176.1	175.9	193.3	173.8
Resistivity (25 °C) /µ Ohm cm	57–80 20 °C	73	68	64		88	90	134	114	57	87	87	79	29	79
mag susceptibility χ _{mol} /10 ⁻⁶ (cm ³ ·mol ⁻¹)	+95.9	+2500 (β)	+5530(α)	+5930 (α)		+1278(α)	+30900	+185000 (350 K)	+170000 (α)	+98000	+72900	+48000	+24700	+67 (β)	+183

*Between initial [Xe] and final 6s² electronic shells



Chemical element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ln ³⁺ electron configuration* ^[10]	4f ⁰	4f ¹	4f ²	4f ³	4f ⁴	4f ⁵	4f ⁶	4f ⁷	4f ⁸	4f ⁹	4f ¹⁰	4f ¹¹	4f ¹²	4f ¹³	4f ¹⁴
Ln ³⁺ radius (pm) ^[8]	103	102	99	98.3	97	95.8	94.7	93.8	92.3	91.2	90.1	89	88	86.8	86.1
Ln ⁴⁺ ion colour in aqueous solution ^[11]	—	Orange-yellow	Yellow	Blue-violet	—	—	—	—	Red-brown	Orange-yellow	—	—	—	—	—
Ln ³⁺ ion colour in aqueous solution ^[10]	Colorless	Colorless	Green	Violet	Pink	Pale yellow	Colorless	Colorless	V. pale pink	Pale yellow	Yellow	Rose	Pale green	Colorless	Colorless
Ln ²⁺ ion colour in aqueous solution ^[8]	—	—	—	—	—	Blood red	Colorless	—	—	—	—	—	Violet-red	Yellow-green	—

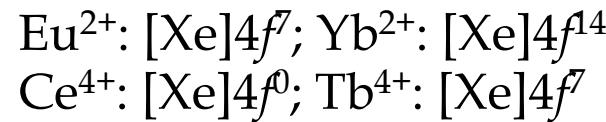


Sc	4s ² 3d ¹	3d ¹
Ti	4s ² 3d ²	3d ²
V	4s ² 3d ³	3d ³
Cr	4s ¹ 3d ⁵	3d ⁴
Mn	4s ² 3d ⁵	3d ⁵
Fe	4s ² 3d ⁶	3d ⁶
Co	4s ² 3d ⁷	3d ⁷
Ni	4s ² 3d ⁸	3d ⁸
Cu	4s ¹ 3d ¹⁰	3d ⁹

Chemical element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ln ³⁺ electron configuration ^[10]	4f ⁰	4f ¹	4f ²	4f ³	4f ⁴	4f ⁵	4f ⁶	4f ⁷	4f ⁸	4f ⁹	4f ¹⁰	4f ¹¹	4f ¹²	4f ¹³	4f ¹⁴
Ln ³⁺ radius (pm) ^[8]	103	102	99	98.3	97	95.8	94.7	93.8	92.3	91.2	90.1	89	88	86.8	86.1
Ln ⁴⁺ ion colour in aqueous solution ^[11]	—	Orange-yellow	Yellow	Blue-violet	—	—	—	—	Red-brown	Orange-yellow	—	—	—	—	—
Ln ³⁺ ion colour in aqueous solution ^[10]	Colorless	Colorless	Green	Violet	Pink	Pale yellow	Colorless	Colorless	V. pale pink	Pale yellow	Yellow	Rose	Pale green	Colorless	Colorless
Ln ²⁺ ion colour in aqueous solution ^[8]	—	—	—	—	—	Blood red	Colorless	—	—	—	—	—	Violet-red	Yellow-green	—

Schematic Energy Levels for Transition Elements.

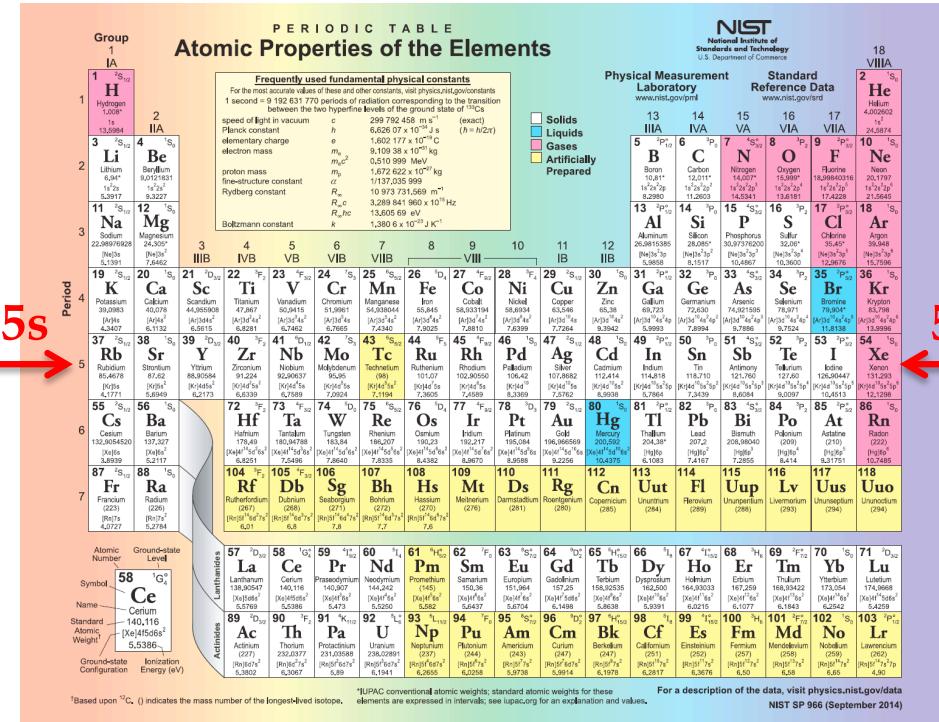
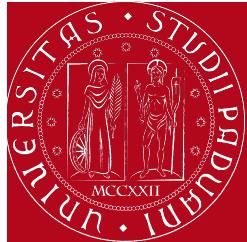
- Schematic interpretation of electron configurations for transition elements in terms of intra-orbital repulsion and trends in subshell energies.
- A similar diagram for ions, showing the shift in the crossover points on removal of an electron. The shift is even more pronounced for metal ions having 2+ or greater charges. As a consequence, transition-metal ions with 2+ or greater charges have no s electrons, only d electrons in their outer levels. Similar diagrams, although more complex, can be drawn for the heavier transition elements and the lanthanides.





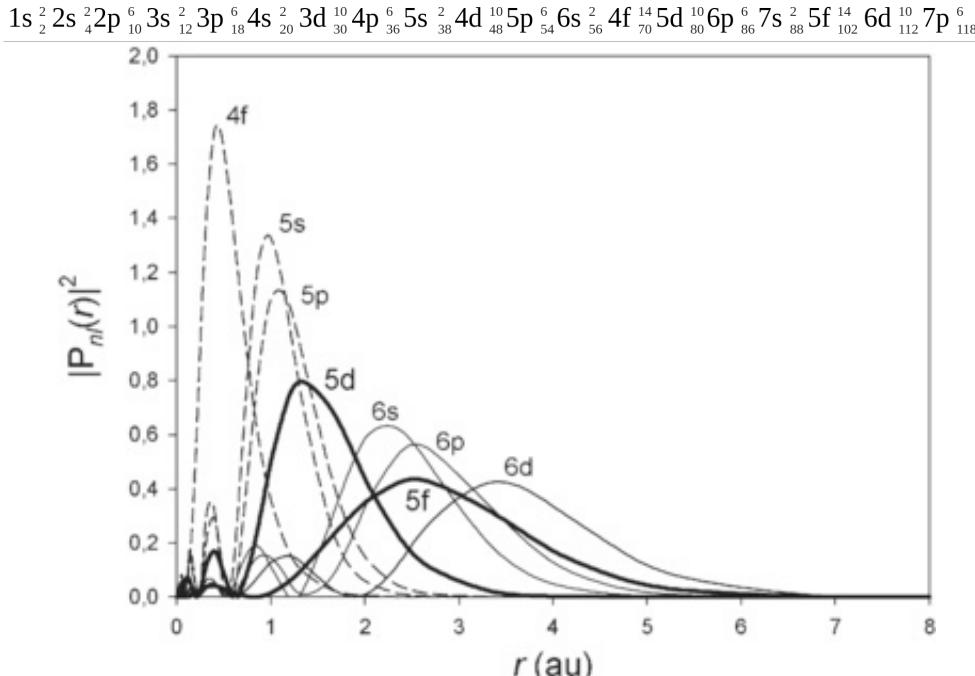
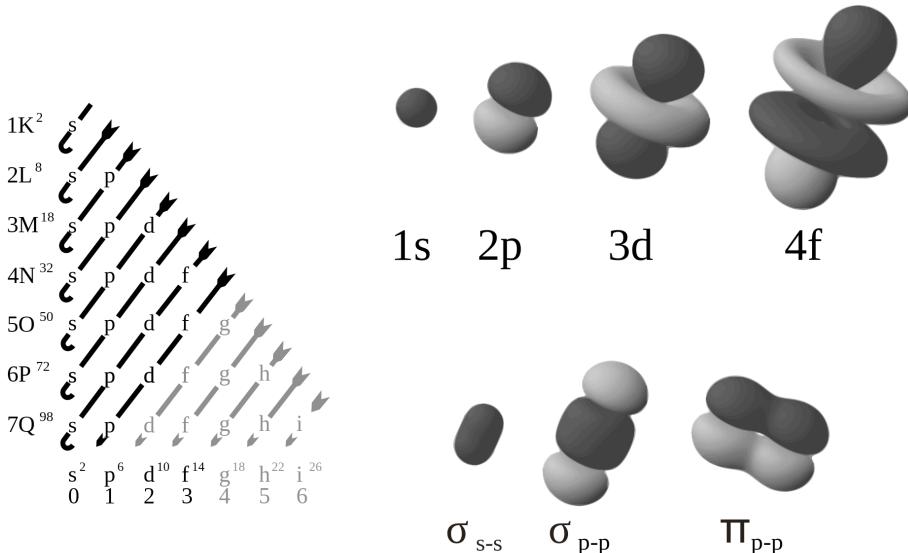
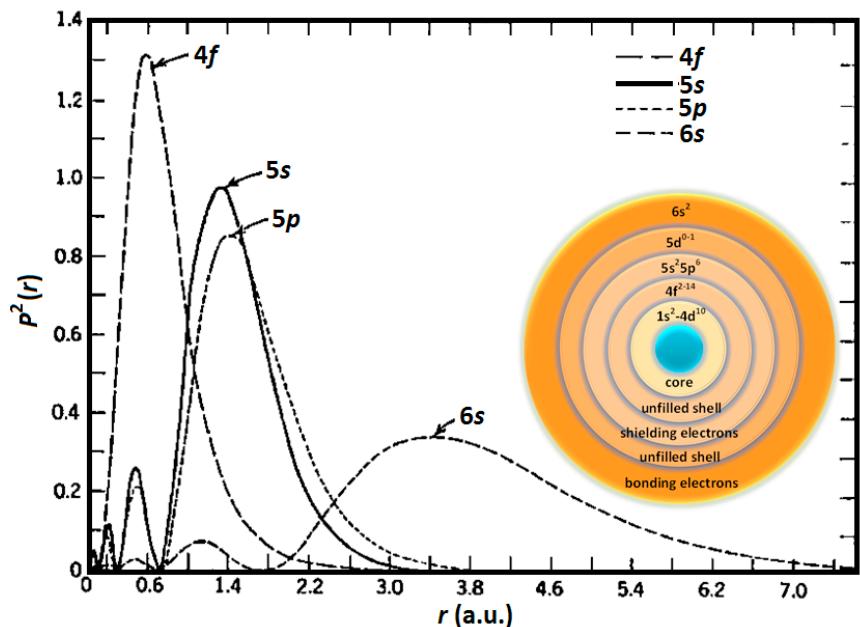
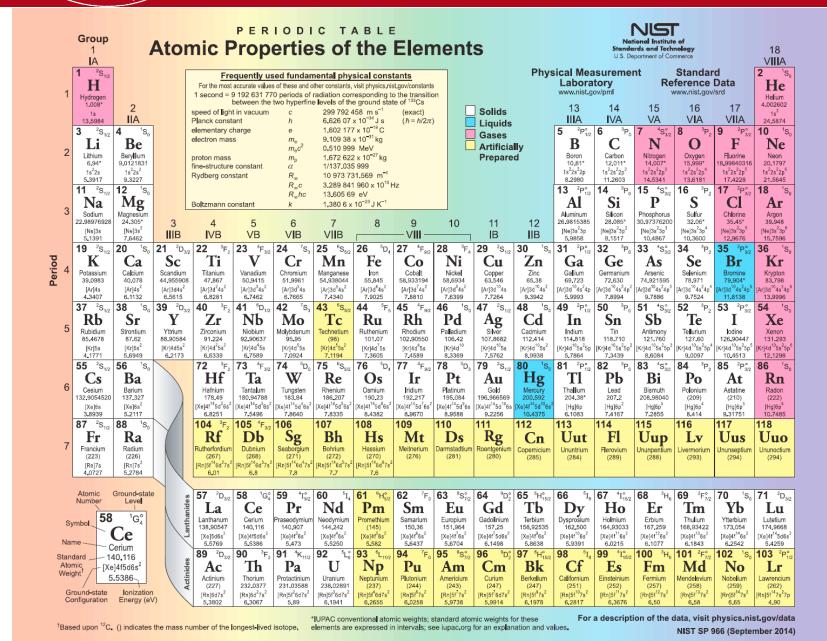
Atomic number	Name	Symbol	Isolated atom electron configuration	M ³⁺ f electron configuration
57	Lanthanum	La	5d ¹ 6s ²	4f ⁰
58	Cerium	Ce	4f ¹ 5d ¹ 6s ²	4f ¹
59	Praseodymium	Pr	4f ³ 6s ²	4f ²
60	Neodymium	Nd	4f ⁴ 6s ²	4f ³
61	Promethium	Pm	4f ⁵ 6s ²	4f ⁴
62	Samarium	Sm	4f ⁶ 6s ²	4f ⁵
63	Europium	Eu	4f ⁷ 6s ²	4f ⁶
64	Gadolinium	Gd	4f ⁷ 5d ¹ 6s ²	4f ⁷
65	Terbium	Tb	4f ⁹ 6s ²	4f ⁸
66	Dysprosium	Dy	4f ¹⁰ 6s ²	4f ⁹
67	Holmium	Ho	4f ¹¹ 6s ²	4f ¹⁰
68	Erbium	Er	4f ¹² 6s ²	4f ¹¹
69	Thulium	Tb	4f ¹³ 6s ²	4f ¹²
70	Ytterbium	Yb	4f ¹⁴ 6s ²	4f ¹³
71	Lutecium	Lu	4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴

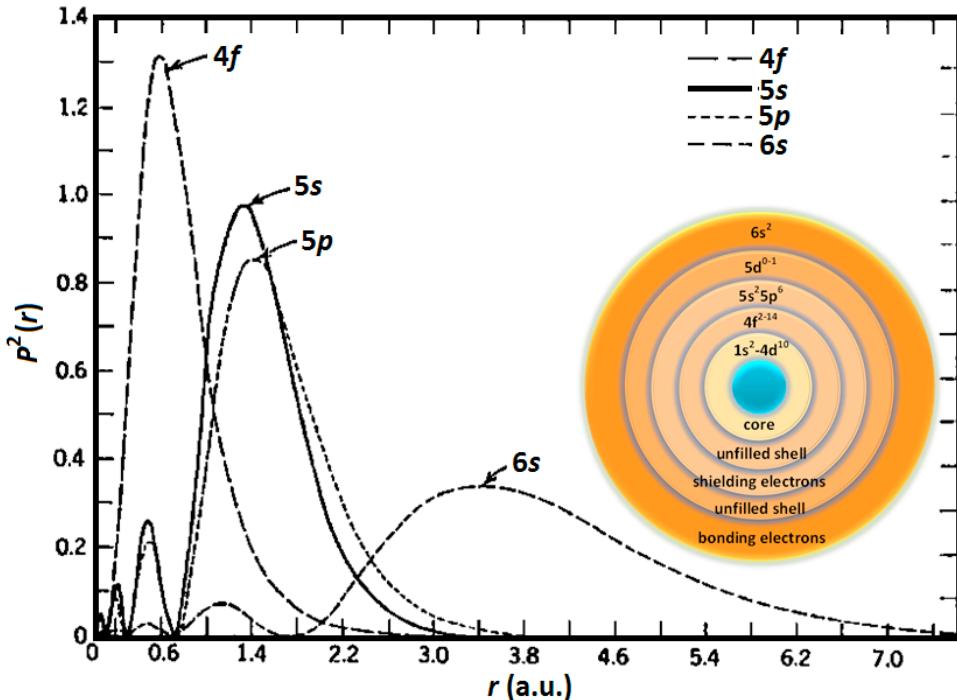
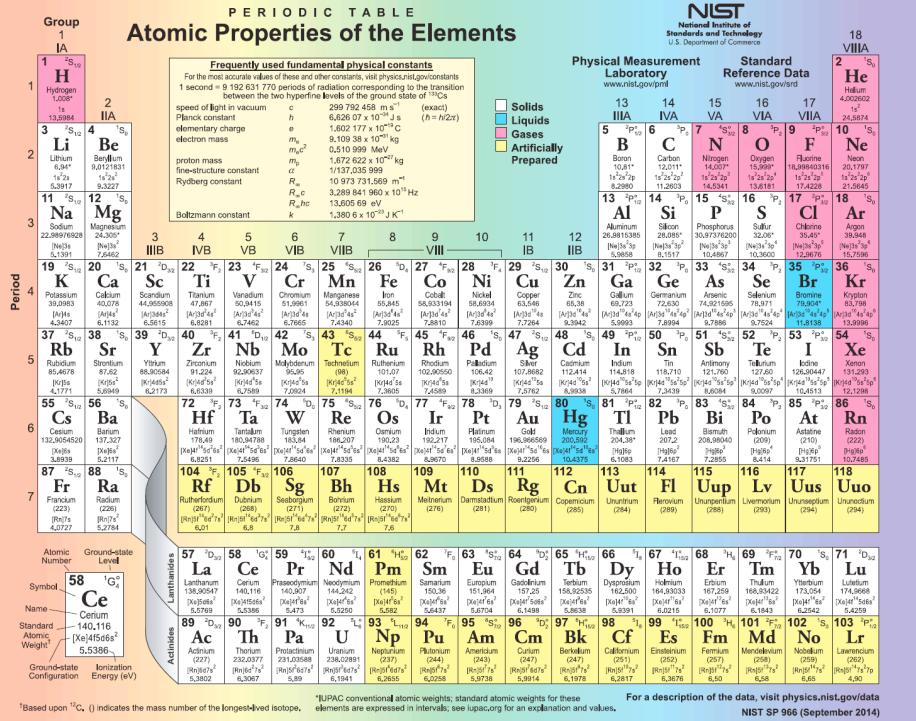
Note: Promethium, effectively, does not occur in nature. It is a fission product of uranium and may be made, for example, by neutron bombardment of neodymium to give an isotope with a half-life of just under 4 years.





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$$Y_{3,-3} = f_{y(3x^2-y^2)} = i\sqrt{\frac{1}{2}} (Y_3^{-3} + Y_3^3) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{(3x^2 - y^2) y}{r^3}$$

$$Y_{3,-2} = f_{xyz} = i\sqrt{\frac{1}{2}} (Y_3^{-2} - Y_3^2) = \frac{1}{2}\sqrt{\frac{105}{\pi}} \cdot \frac{xyz}{r^3}$$

$$Y_{3,-1} = f_{yz^2} = i\sqrt{\frac{1}{2}} (Y_3^{-1} + Y_3^1) = \frac{1}{4}\sqrt{\frac{21}{2\pi}} \cdot \frac{y(4z^2 - x^2 - y^2)}{r^3}$$

$$Y_{30} = f_z = Y_3^0 = \frac{1}{4}\sqrt{\frac{7}{\pi}} \cdot \frac{z(2z^2 - 3x^2 - 3y^2)}{r^3}$$

$$Y_{31} = f_{xz^2} = \sqrt{\frac{1}{2}} (Y_3^{-1} - Y_3^1) = \frac{1}{4}\sqrt{\frac{21}{2\pi}} \cdot \frac{x(4z^2 - x^2 - y^2)}{r^3}$$

$$Y_{32} = f_{z(x^2-y^2)} = \sqrt{\frac{1}{2}} (Y_3^{-2} + Y_3^2) = \frac{1}{4}\sqrt{\frac{105}{\pi}} \cdot \frac{(x^2 - y^2) z}{r^3}$$

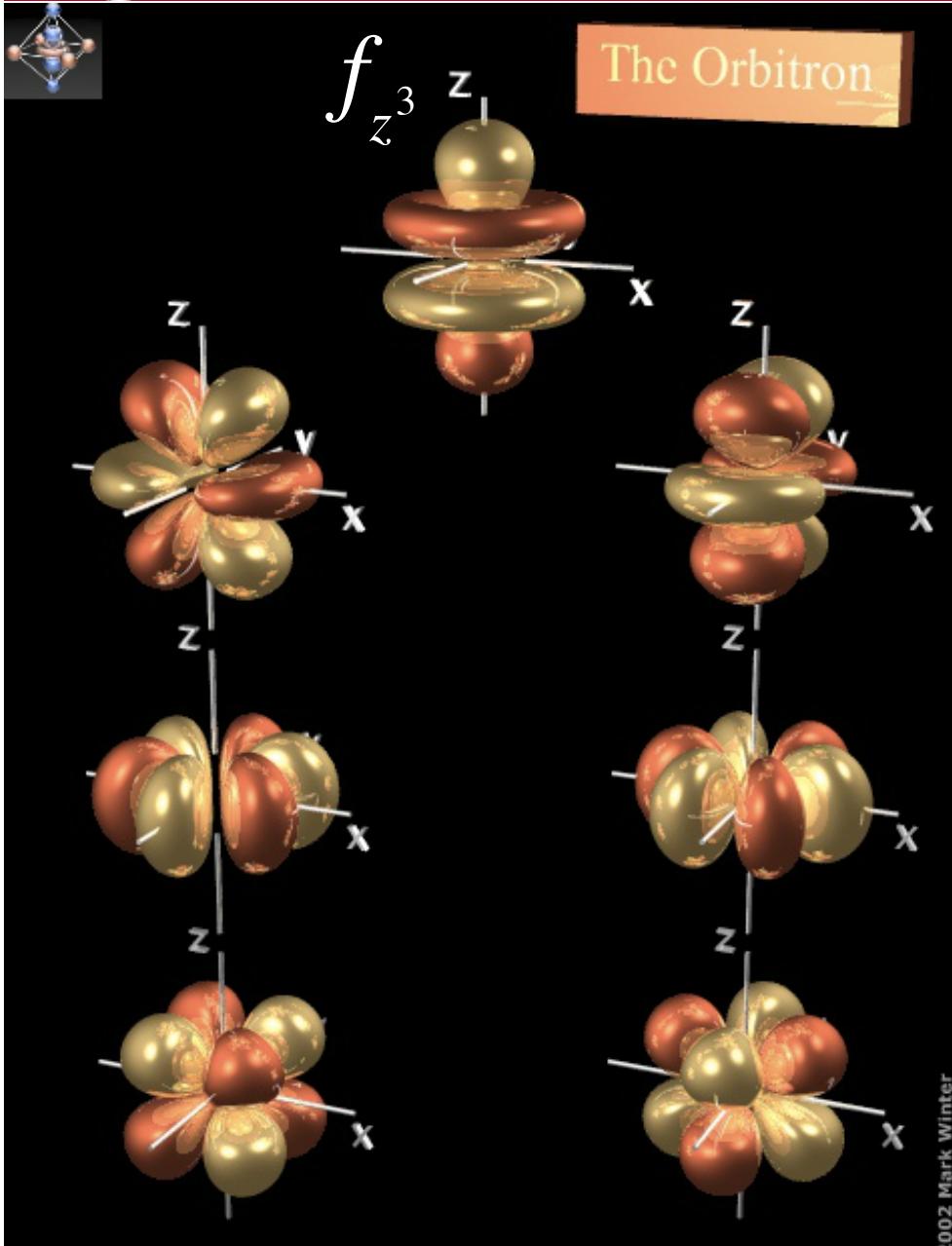
$$Y_{33} = f_{x(x^2-3y^2)} = \sqrt{\frac{1}{2}} (Y_3^{-3} - Y_3^3) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{(x^2 - 3y^2) x}{r^3}$$



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$$\rho_n \equiv \frac{2Z}{a_0 n} r$$
$$R_{43}(r) = \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} \frac{1}{96\sqrt{35}} \rho_n^3$$



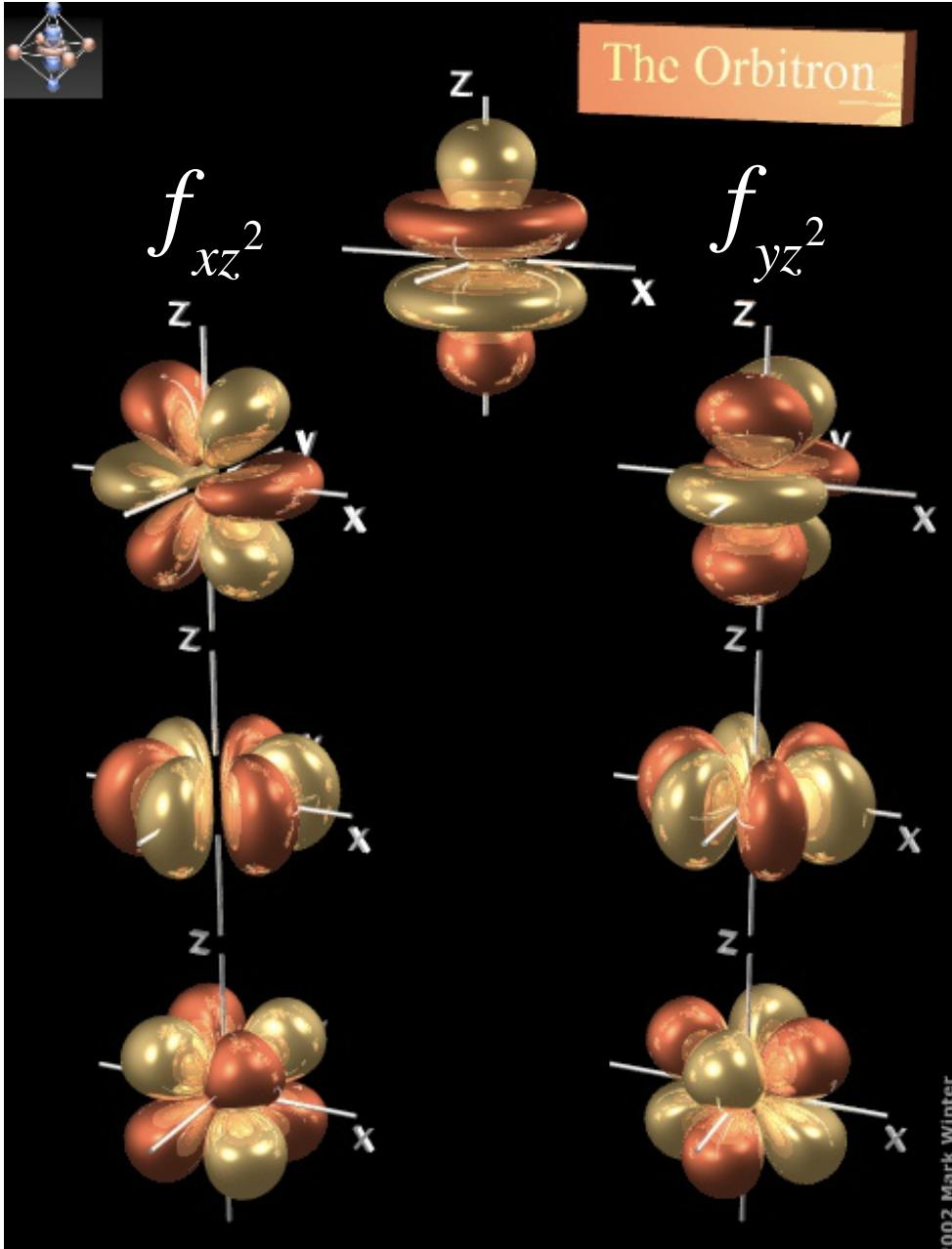
$$Y_{30} = f_{z^3} = Y_3^0 = \frac{1}{4} \sqrt{\frac{7}{\pi}} \cdot \frac{z(2z^2 - 3x^2 - 3y^2)}{r^3}$$



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$$Y_{31} = f_{xz^2} = \sqrt{\frac{1}{2}} (Y_3^{-1} - Y_3^1) = \frac{1}{4} \sqrt{\frac{21}{2\pi}} \cdot \frac{x(4z^2 - x^2 - y^2)}{r^3}$$

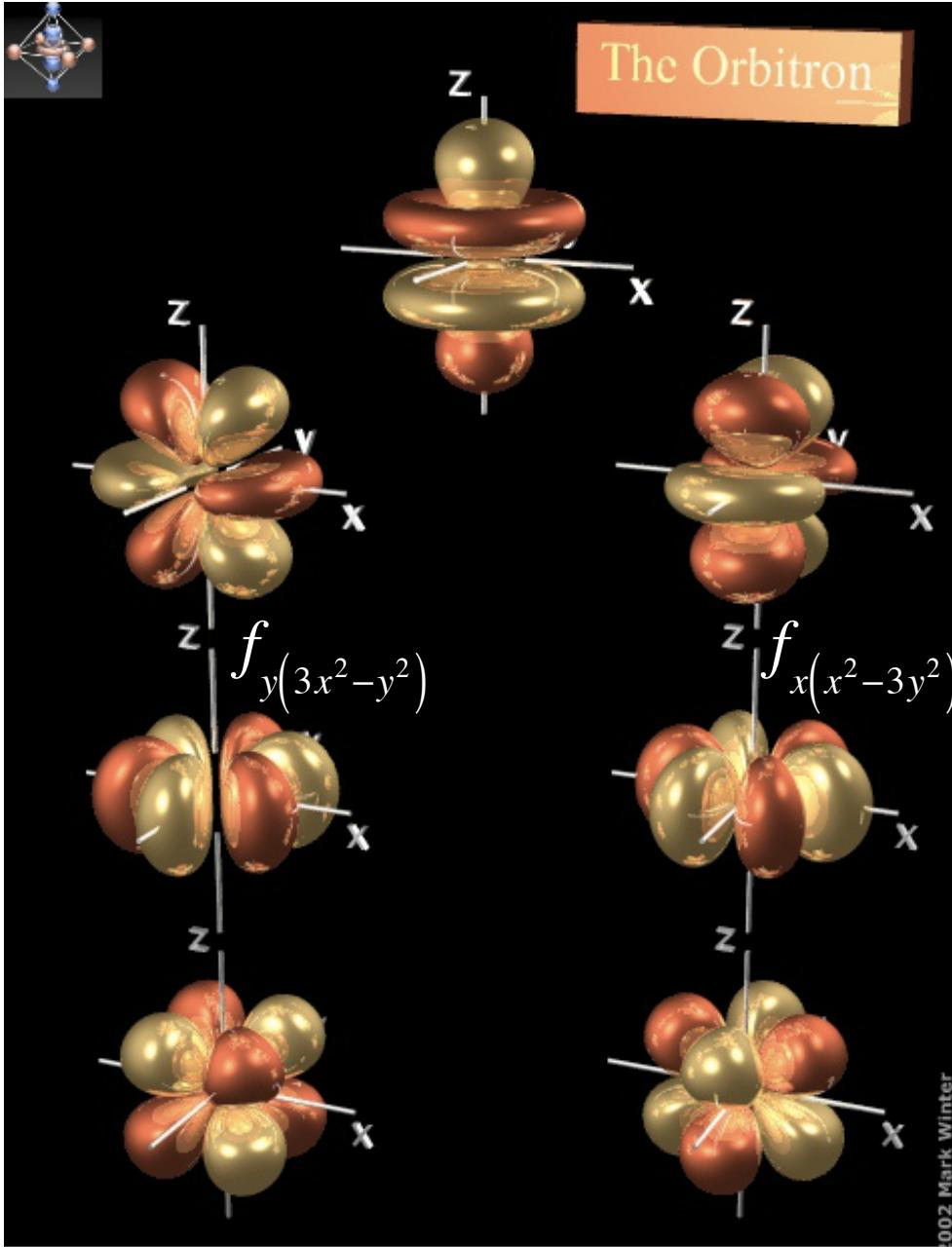
$$Y_{3,-1} = f_{yz^2} = i\sqrt{\frac{1}{2}} (Y_3^{-1} + Y_3^1) = \frac{1}{4} \sqrt{\frac{21}{2\pi}} \cdot \frac{y(4z^2 - x^2 - y^2)}{r^3}$$



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$$\rho_n \equiv \frac{2Z}{a_0 n} r$$
$$R_{43}(r) = \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} \frac{1}{96\sqrt{35}} \rho_n^3$$



$$Y_{3,-3} = f_{y(3x^2-y^2)} = i\sqrt{\frac{1}{2}} (Y_3^{-3} + Y_3^3) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{(3x^2 - y^2) y}{r^3}$$

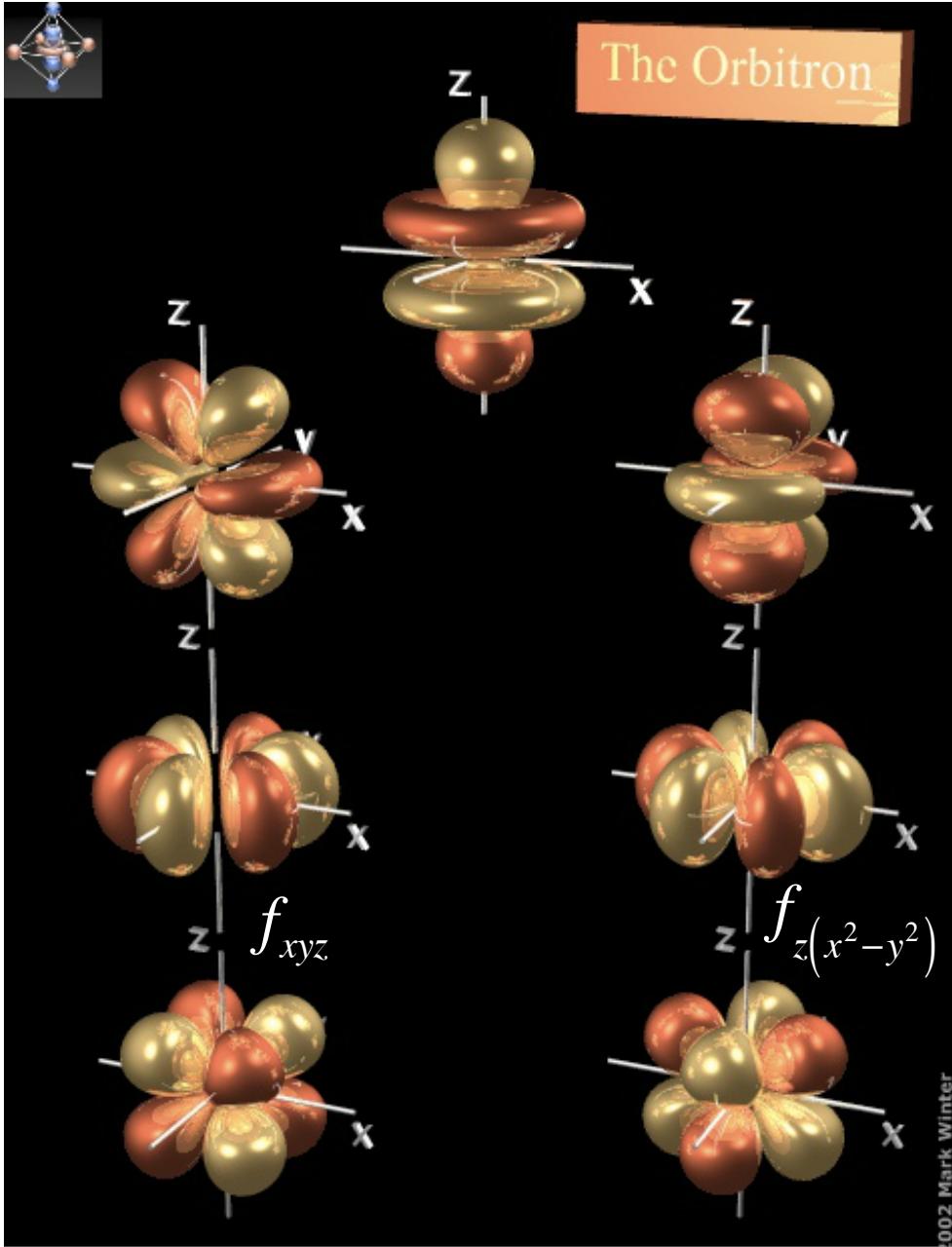
$$Y_{33} = f_{x(x^2-3y^2)} = \sqrt{\frac{1}{2}} (Y_3^{-3} - Y_3^3) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{(x^2 - 3y^2) x}{r^3}$$



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$$\rho_n \equiv \frac{2Z}{a_0 n} r$$
$$R_{43}(r) = \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} \frac{1}{96\sqrt{35}} \rho_n^3$$



$$Y_{3,-2} = f_{xyz} = i \sqrt{\frac{1}{2}} (Y_3^{-2} - Y_3^2) = \frac{1}{2} \sqrt{\frac{105}{\pi}} \cdot \frac{xyz}{r^3}$$

$$Y_{32} = f_{z(x^2-y^2)} = \sqrt{\frac{1}{2}} (Y_3^{-2} + Y_3^2) = \frac{1}{4} \sqrt{\frac{105}{\pi}} \cdot \frac{(x^2 - y^2) z}{r^3}$$



$$\rho_n \equiv \frac{2Z}{a_0 n} r$$

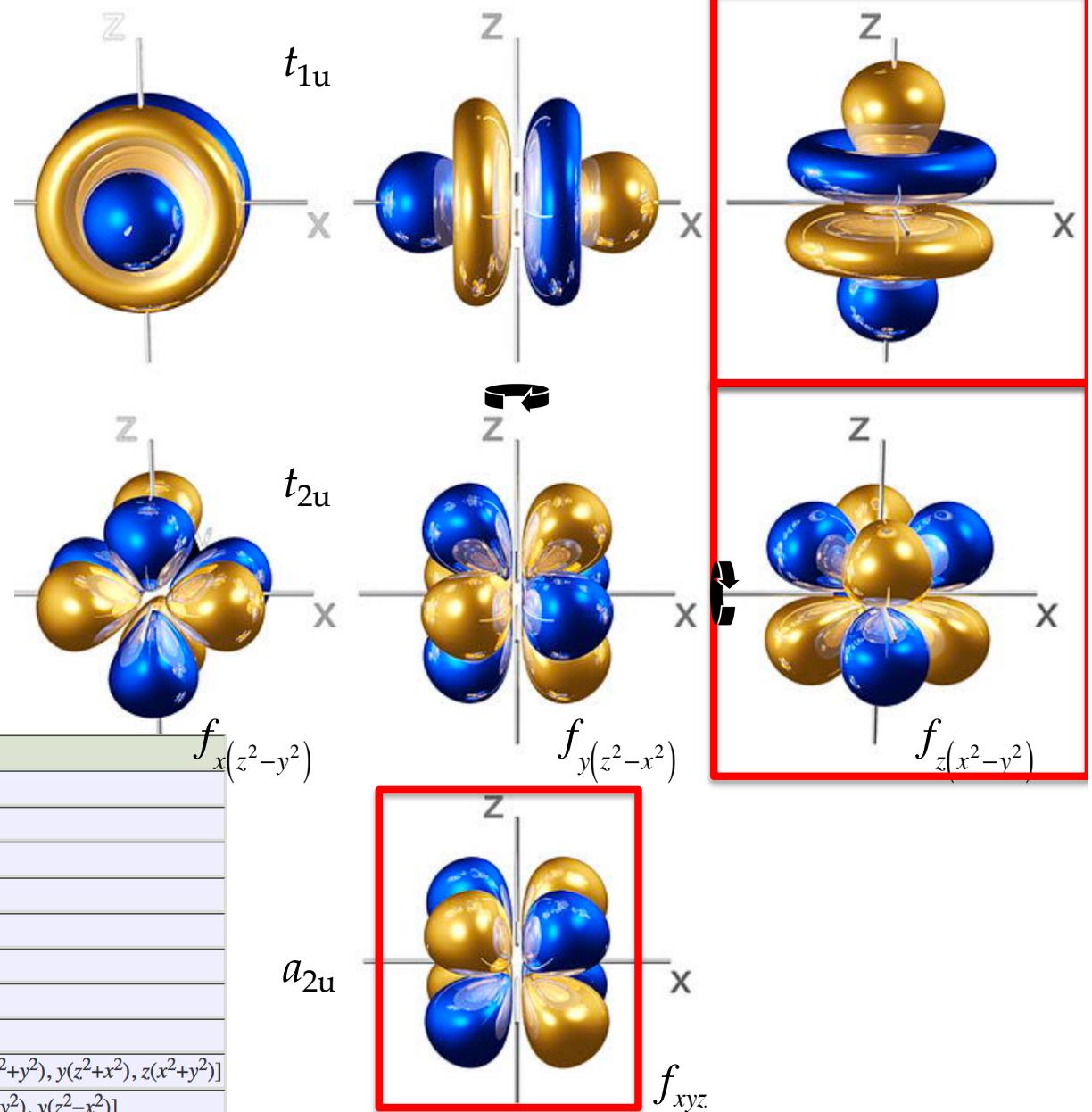
$$R_{43}(r) = \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} \frac{1}{96\sqrt{35}} \rho_n^3$$

$$t_{1u} : \begin{cases} f_{x^3} = -\frac{1}{4} [\sqrt{6}Y_{31} - \sqrt{10}Y_{33}] \\ f_{y^3} = -\frac{1}{4} [\sqrt{6}Y_{3-1} + \sqrt{10}Y_{3-3}] \\ f_{z^3} = f_{z^3} \end{cases}$$

$$t_{2u} : \begin{cases} f_{z(x^2-y^2)} = f_{z(x^2-y^2)} \\ f_{x(z^2-y^2)} = \frac{1}{4} [\sqrt{10}Y_{31} + \sqrt{6}Y_{33}] \\ f_{y(z^2-x^2)} = \frac{1}{4} [\sqrt{10}Y_{3-1} - \sqrt{6}Y_{3-3}] \end{cases}$$

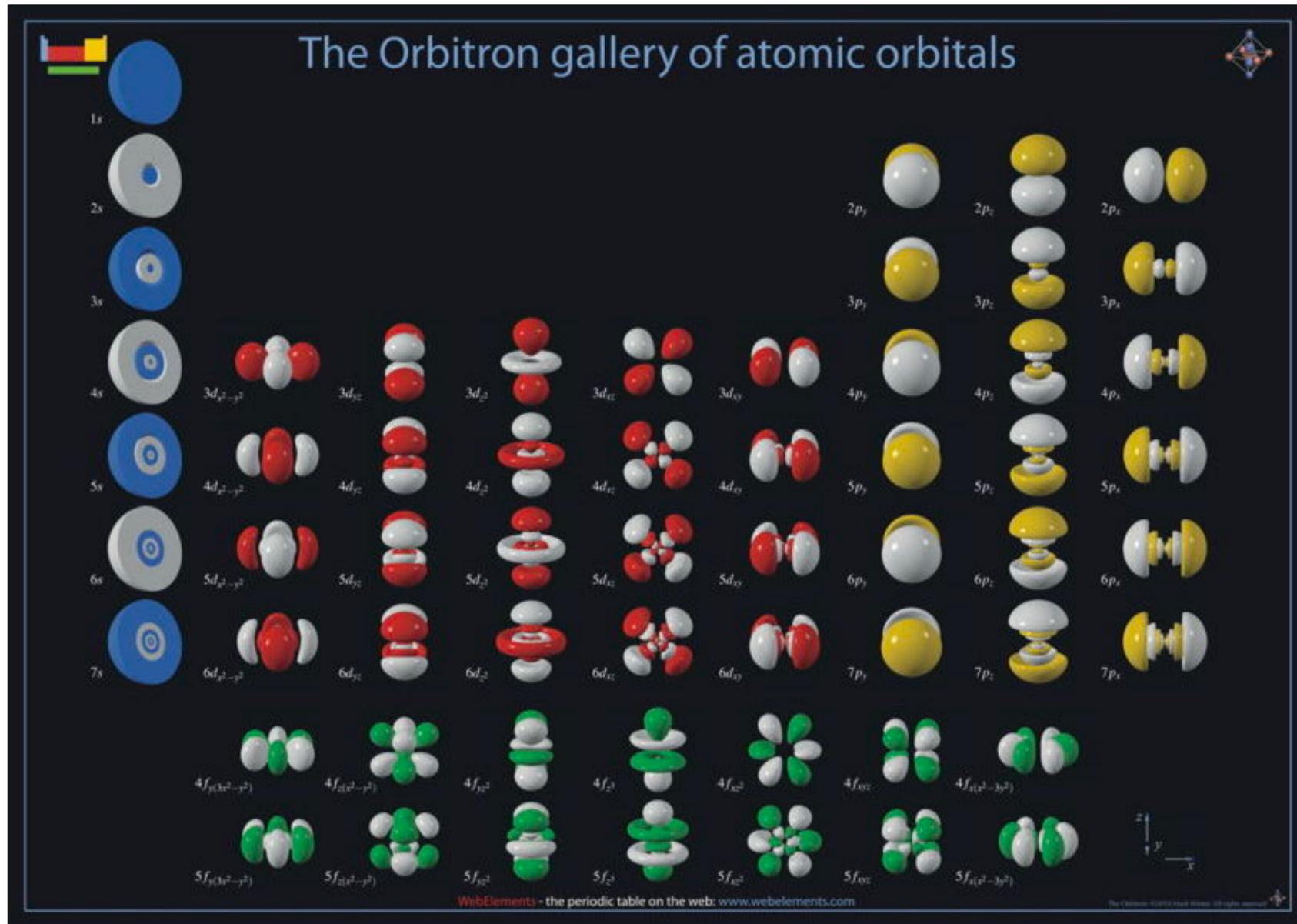
$$a_{2u} : \{ f_{xyz} = f_{xyz} \}$$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2'$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Cubic
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	xyz
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	$(x^3, y^3, z^3); [x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	$[x(y^2-z^2), z(x^2-y^2), y(z^2-x^2)]$





<https://www.webelements.com/shop/product/orbitron-atomic-orbitals-poster/>

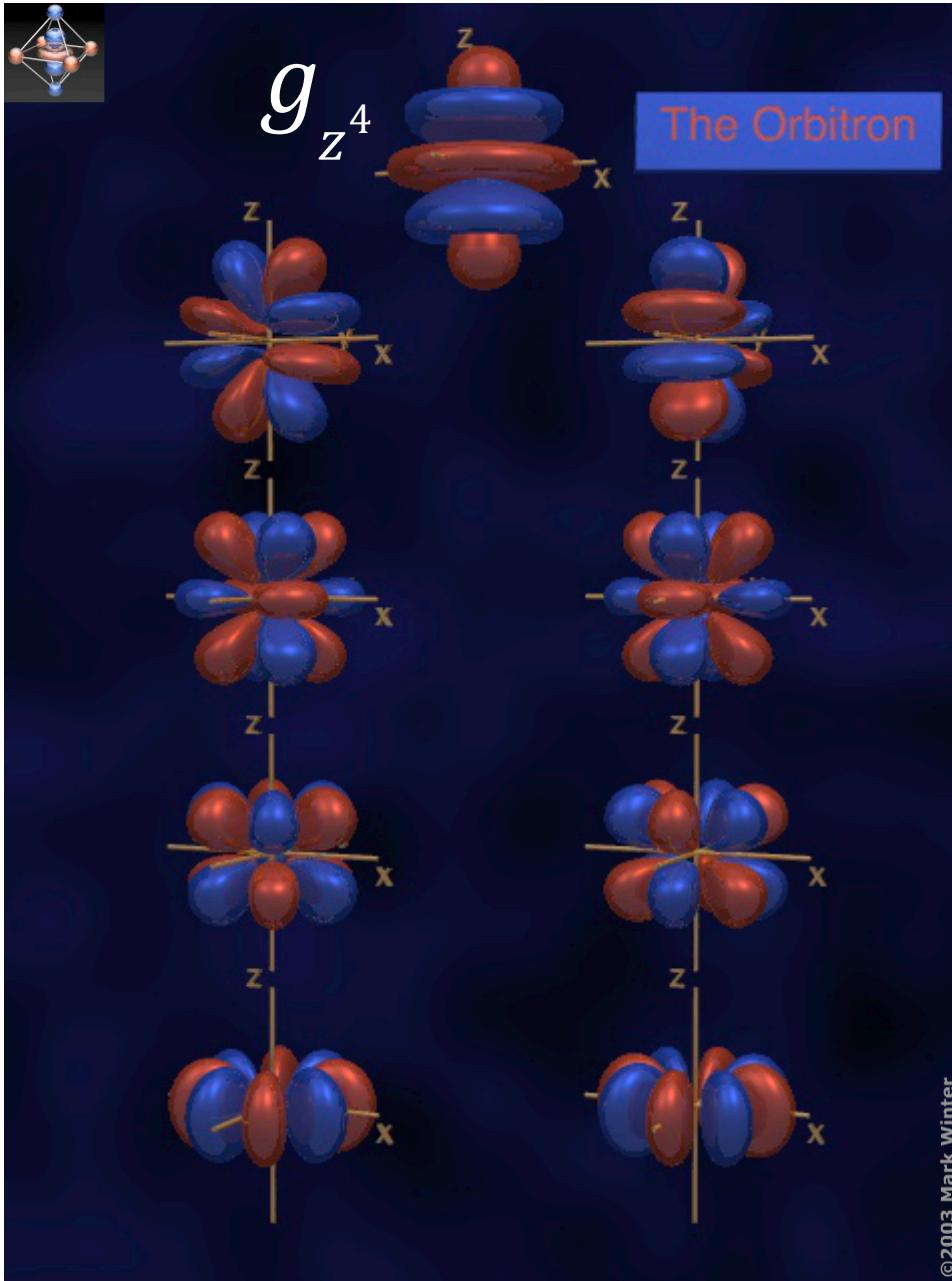




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$$\rho_n \equiv \frac{2Z}{a_0 n} r$$
$$R_{54} = \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} - \frac{1}{900\sqrt{70}} \rho_n^4$$



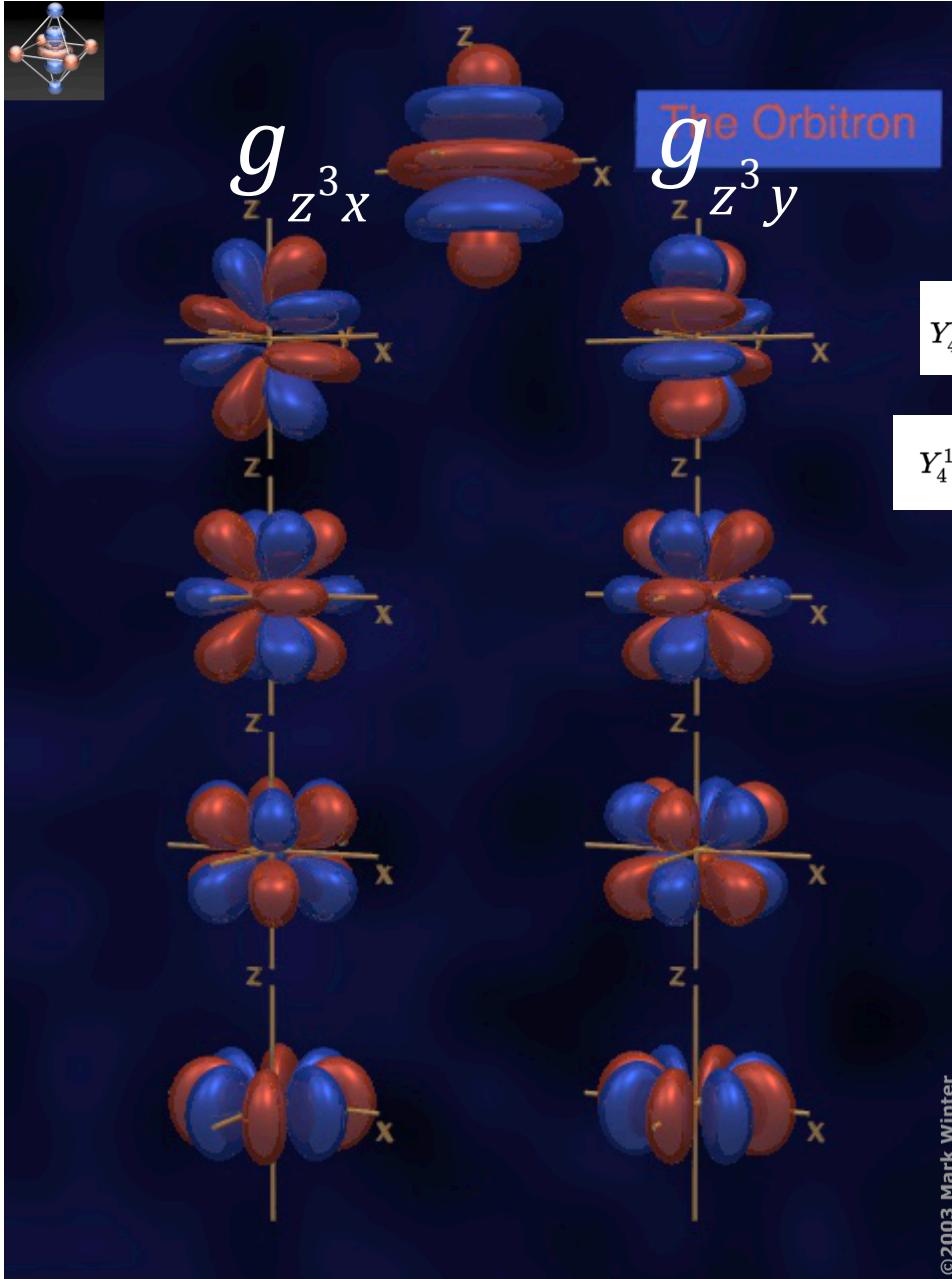
$$Y_4^0(\theta, \varphi) = \frac{3}{16} \sqrt{\frac{1}{\pi}} \cdot (35 \cos^4 \theta - 30 \cos^2 \theta + 3) = \frac{3}{16} \sqrt{\frac{1}{\pi}} \cdot \frac{(35z^4 - 30z^2r^2 + 3r^4)}{r^4}$$



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$$Y_4^{-1}(\theta, \varphi) = \frac{3}{8} \sqrt{\frac{5}{\pi}} \cdot e^{-i\varphi} \cdot \sin \theta \cdot (7 \cos^3 \theta - 3 \cos \theta) = \frac{3}{8} \sqrt{\frac{5}{\pi}} \cdot \frac{(x - iy) \cdot z \cdot (7z^2 - 3r^2)}{r^4}$$

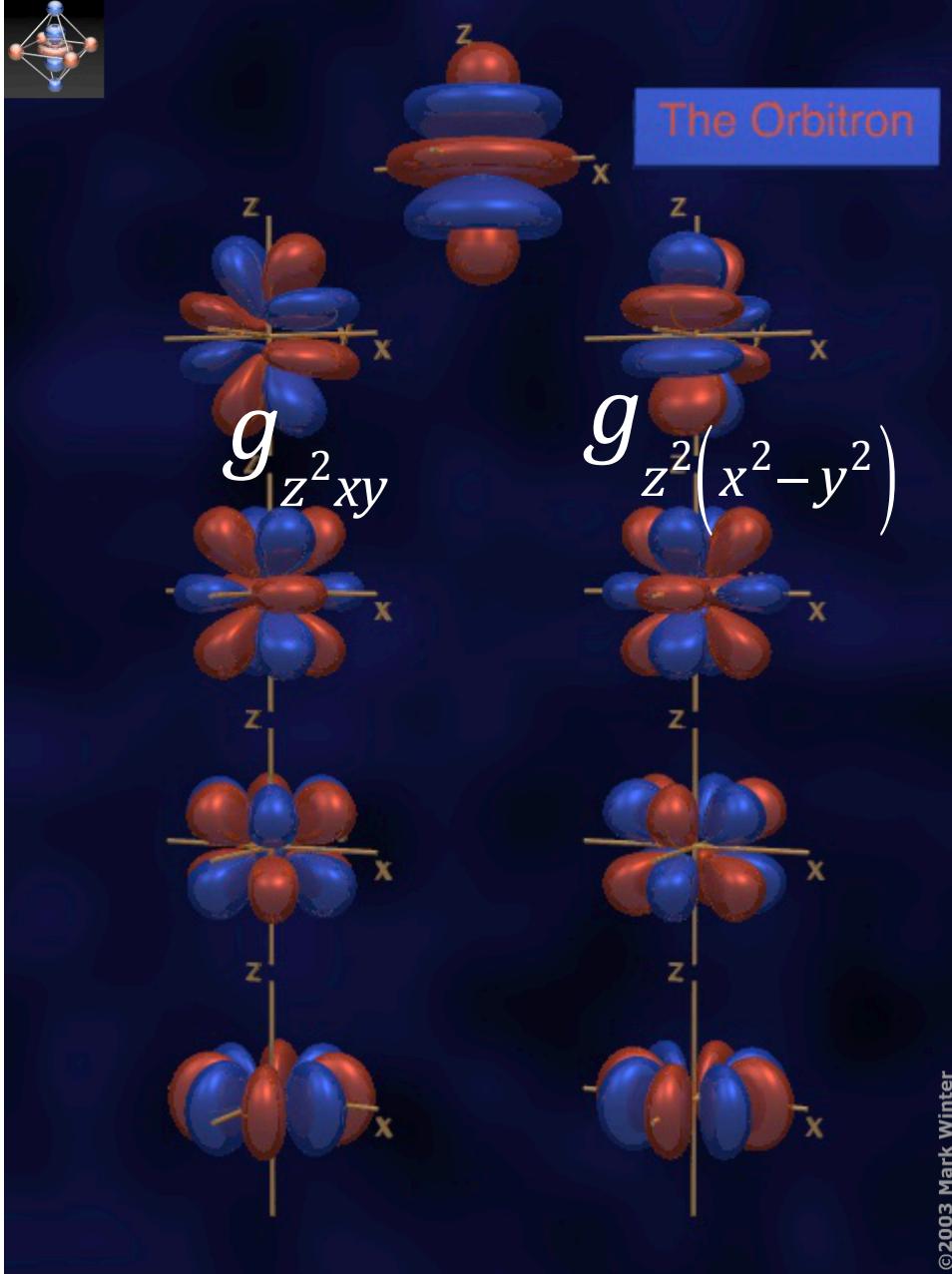
$$Y_4^1(\theta, \varphi) = \frac{-3}{8} \sqrt{\frac{5}{\pi}} \cdot e^{i\varphi} \cdot \sin \theta \cdot (7 \cos^3 \theta - 3 \cos \theta) = \frac{-3}{8} \sqrt{\frac{5}{\pi}} \cdot \frac{(x + iy) \cdot z \cdot (7z^2 - 3r^2)}{r^4}$$



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$$\rho_n \equiv \frac{2Z}{a_0 n} r$$
$$R_{54} = \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} - \frac{1}{900\sqrt{70}} \rho_n^4$$



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$$Y_4^{-2}(\theta, \varphi) = \frac{3}{8} \sqrt{\frac{5}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2 \theta \cdot (7 \cos^2 \theta - 1) = \frac{3}{8} \sqrt{\frac{5}{2\pi}} \cdot \frac{(x - iy)^2 \cdot (7z^2 - r^2)}{r^4}$$

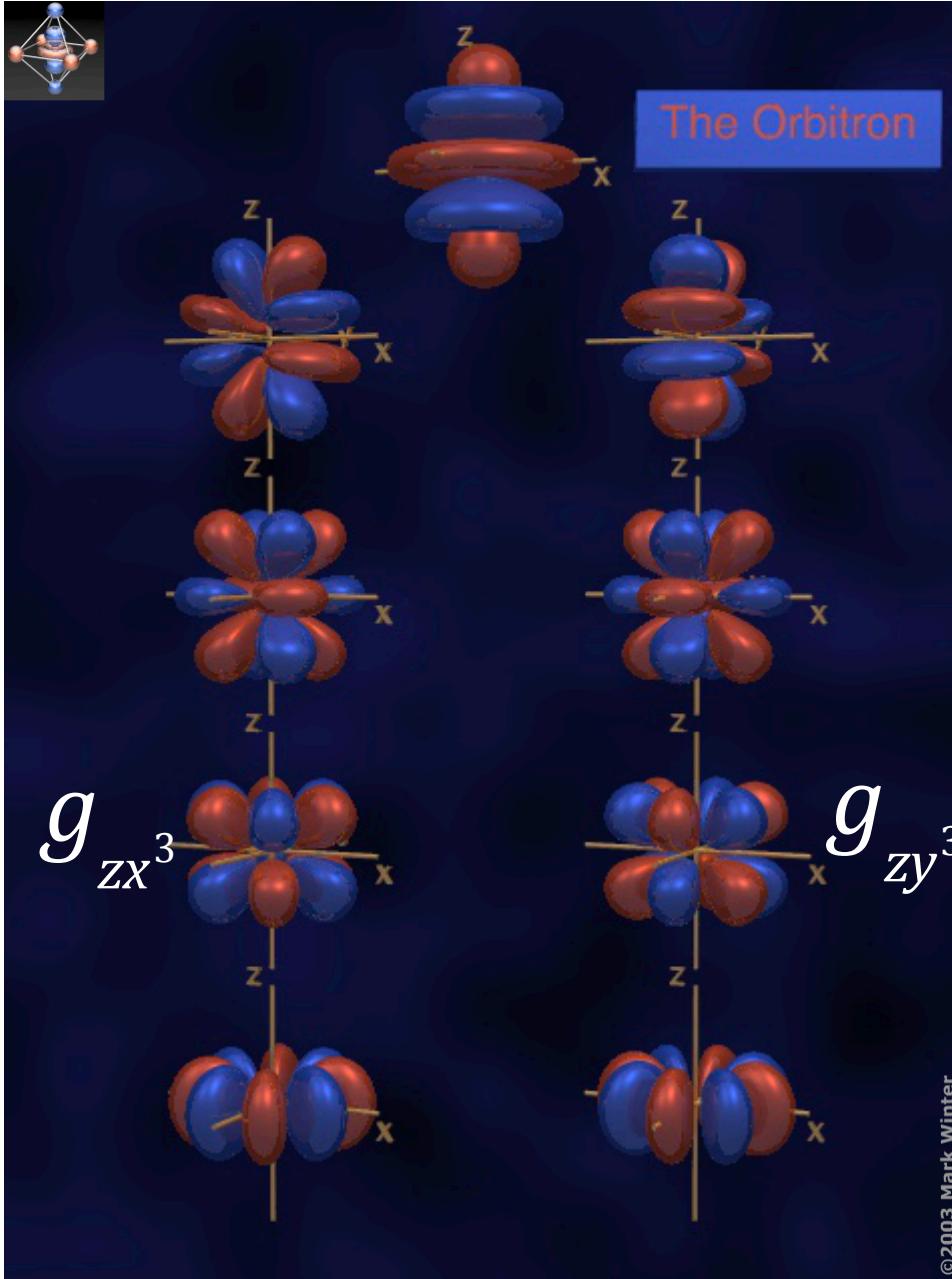
$$Y_4^2(\theta, \varphi) = \frac{3}{8} \sqrt{\frac{5}{2\pi}} \cdot e^{2i\varphi} \cdot \sin^2 \theta \cdot (7 \cos^2 \theta - 1) = \frac{3}{8} \sqrt{\frac{5}{2\pi}} \cdot \frac{(x + iy)^2 \cdot (7z^2 - r^2)}{r^4}$$



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$$\rho_n \equiv \frac{2Z}{a_0 n} r$$
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$$Y_4^{-3}(\theta, \varphi) = \frac{3}{8} \sqrt{\frac{35}{\pi}} \cdot e^{-3i\varphi} \cdot \sin^3 \theta \cdot \cos \theta = \frac{3}{8} \sqrt{\frac{35}{\pi}} \cdot \frac{(x - iy)^3 z}{r^4}$$

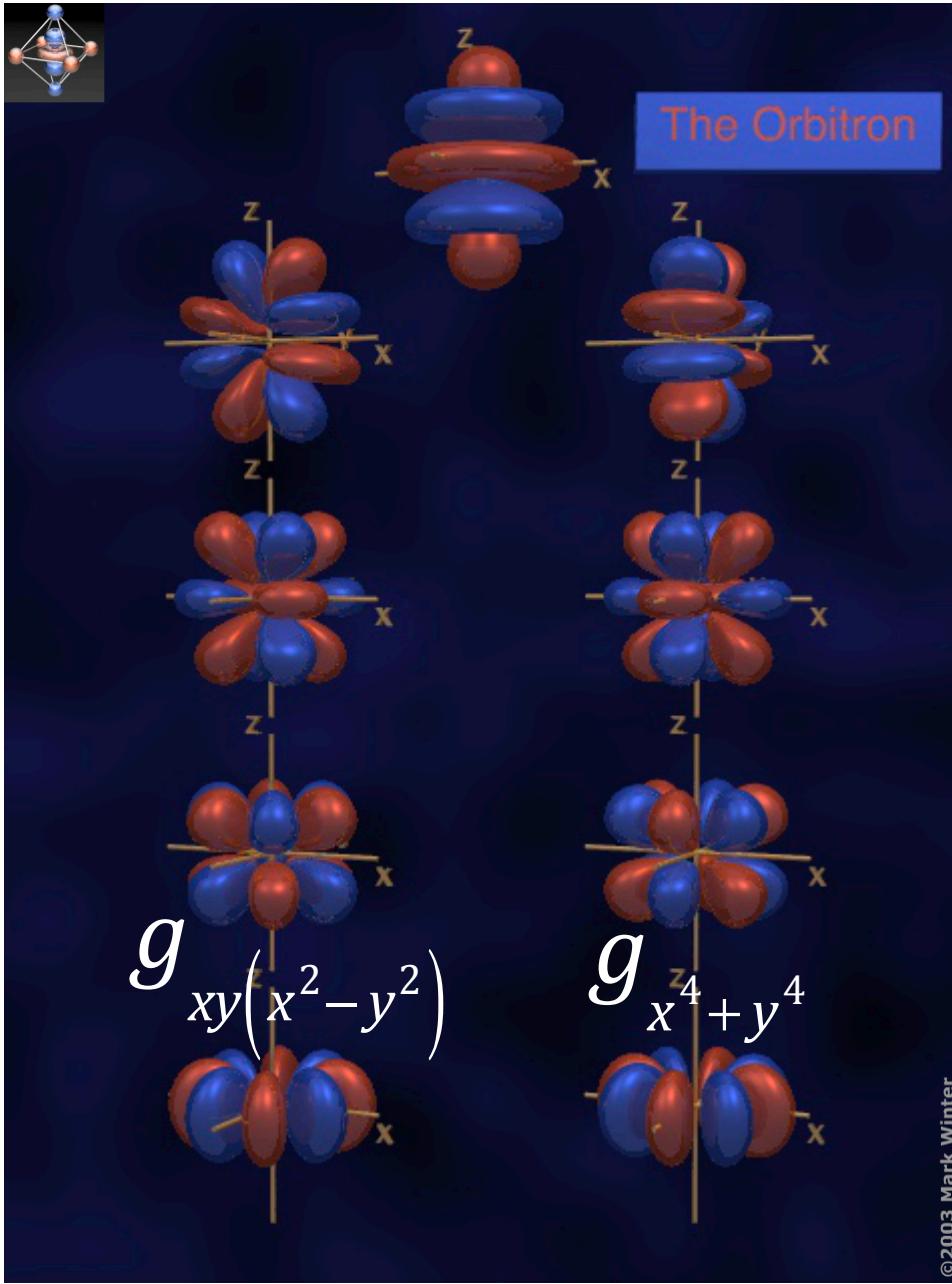
$$Y_4^3(\theta, \varphi) = \frac{-3}{8} \sqrt{\frac{35}{\pi}} \cdot e^{3i\varphi} \cdot \sin^3 \theta \cdot \cos \theta = \frac{-3}{8} \sqrt{\frac{35}{\pi}} \cdot \frac{(x + iy)^3 z}{r^4}$$



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$$\rho_n \equiv \frac{2Z}{a_0 n} r$$
$$R_{54} = \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} - \frac{1}{900\sqrt{70}} \rho_n^4$$

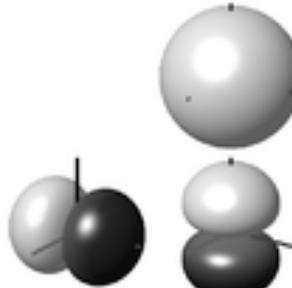


$$Y_4^{-4}(\theta, \varphi) = \frac{3}{16} \sqrt{\frac{35}{2\pi}} \cdot e^{-4i\varphi} \cdot \sin^4 \theta = \frac{3}{16} \sqrt{\frac{35}{2\pi}} \cdot \frac{(x - iy)^4}{r^4}$$

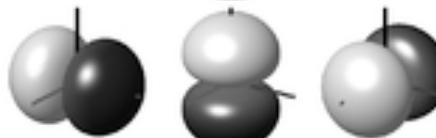
$$Y_4^4(\theta, \varphi) = \frac{3}{16} \sqrt{\frac{35}{2\pi}} \cdot e^{4i\varphi} \cdot \sin^4 \theta = \frac{3}{16} \sqrt{\frac{35}{2\pi}} \cdot \frac{(x + iy)^4}{r^4}$$



$\ell = 0 (s)$



$\ell = 1 (p)$



$\ell = 2 (d)$



$\ell = 3 (f)$



$\ell = 4 (g)$



$\ell = 5 (h)$

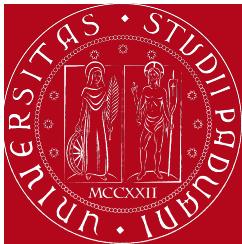


Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.



Atomic number	Name	Symbol	Isolated atom electron configuration	M ³⁺ f electron configuration
57	Lanthanum	La	5d ¹ 6s ²	4f ⁰
58	Cerium	Ce	4f ¹ 5d ¹ 6s ²	4f ¹
59	Praseodymium	Pr	4f ³ 6s ²	4f ²
60	Neodymium	Nd	4f ⁴ 6s ²	4f ³
61	Promethium	Pm	4f ⁵ 6s ²	4f ⁴
62	Samarium	Sm	4f ⁶ 6s ²	4f ⁵
63	Europium	Eu	4f ⁷ 6s ²	4f ⁶
64	Gadolinium	Gd	4f ⁷ 5d ¹ 6s ²	4f ⁷
65	Terbium	Tb	4f ⁹ 6s ²	4f ⁸
66	Dysprosium	Dy	4f ¹⁰ 6s ²	4f ⁹
67	Holmium	Ho	4f ¹¹ 6s ²	4f ¹⁰
68	Erbium	Er	4f ¹² 6s ²	4f ¹¹
69	Thulium	Tb	4f ¹³ 6s ²	4f ¹²
70	Ytterbium	Yb	4f ¹⁴ 6s ²	4f ¹³
71	Lutecium	Lu	4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴

Note: Promethium, effectively, does not occur in nature. It is a fission product of uranium and may be made, for example, by neutron bombardment of neodymium to give an isotope with a half-life of just under 4 years.



$4f^1$

$$\ell_1 = 3$$

$$L = \ell_1$$

$$L = 3$$

F

$$s_1 = 1/2$$

$$S = s_1$$

$$2S+1 = 2$$

$m_\ell \setminus m_s$	$1/2$	$-1/2$
3	3^+	3^-
2	2^+	2^-
1	1^+	1^-
0	0^+	0^-
-3	-3^+	-3^-
-2	-2^+	-2^-
-1	-1^+	-1^-

2F

r = radius

$\pi = 3.14159$ approximately

$e = 2.71828$ approximately

Z = effective nuclear charge for that orbital in that atom.

$\rho = 2Zr/a_0 n$ where n is the principal quantum number (4 for the $4f$ orbitals)

$$R_{43}(r) = \frac{1}{96\sqrt{35}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_4}{2}} \rho_4^3$$

$$\rho_4 \equiv \frac{2Z}{a_0} r$$



Ion	Value of L																				
	Symbol of L																				
	S	P	D	F	G	H	I	K	L	M	N	O	Q	R	T	U	V	W	X	Y	Z
f electron configuration	Angular momentum of relevant orbitals					Total orbital angular momentum					Term associated with the ground state										
La ^{III}	f ⁰	none					0					1S									
Ce ^{III}	f ¹	3					3					2F									
Pr ^{III}	f ²	3, 2					5					3H									
Nd ^{III}	f ³	3, 2, 1					6					4I									
Pm ^{III}	f ⁴	3, 2, 1, 0					6					5I									
Sm ^{III}	f ⁵	3, 2, 1, 0, -1					5					6H									
Eu ^{III}	f ⁶	3, 2, 1, 0, -1, -2					3					7F									
Gd ^{III}	f ⁷	3, 2, 1, 0, -1, -2, -3					0					8S									
Tb ^{III}	f ⁸	3 ^a					3					7F									
Dy ^{III}	f ⁹	3, 2					5					6H									
Ho ^{III}	f ¹⁰	3, 2, 1					6					5I									
Er ^{III}	f ¹¹	3, 2, 1, 0					6					4I									
Tm ^{III}	f ¹²	3, 2, 1, 0, -1					5					3H									
Yb ^{III}	f ¹³	3, 2, 1, 0, -1, -2					3					2F									
Lu ^{III}	f ¹⁴	3, 2, 1, 0, -1, -2, -3					0					1S									

^a From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.



Spectral Terms by Spin Factoring

In applying the spin-factoring method, we obtain the *partial terms* for each of the spin set (electrons with $m_s = +1/2$ or $-1/2$ form a spin set). The partial terms of the spin sets (designated α and β) are multiplied to generate the complete terms.

Since an empty, a half-filled, or a filled complete set of orbitals contributes nothing to the orbital angular momentum, corresponding to an S term, an empty spin set or a complete spin set (half-filled orbitals) also gives an S partial term.

One electron in a complete orbital set gives a term with the corresponding label, $s^1 \rightarrow S$, $p^1 \rightarrow P$, $d^1 \rightarrow D$, $f^1 \rightarrow F$, etc., so a spin set (α or β) consisting of one electron gives these same partial terms. The partial terms for various numbers of electrons in a spin set are given for orbitals through g in the following Table.

One vacancy in a spin set (one hole) gives the same partial term as for one electron, P for p_α^1 or p_α^2 ; D for d_α^1 or d_α^4 ; F for f_α^1 or f_α^6 etc.



Partial Terms Arising from the Occupancy of a Single Spin Set^{a,b}

Orbital set	Orbital occupancy (electrons or holes)							
	0	1	2	3	4	5	6	7
<i>s</i>	<i>S</i>	<i>S</i>						
<i>p</i>	<i>S</i>	<i>P</i>	<i>P</i>	<i>S</i>				
<i>d</i>	<i>S</i>	<i>D</i>	<i>PF</i>	<i>PF</i>	<i>D</i>	<i>S</i>		
<i>f</i>	<i>S</i>	<i>F</i>	<i>PFH</i>	<i>SDFGI</i>	<i>SDFGI</i>	<i>PFH</i>	<i>F</i>	<i>S</i>
<i>g</i>	<i>S</i>	<i>G</i>	<i>PFHK</i>	<i>PF[2]G^c</i>	<i>SD[2]FG[2]</i>			
				<i>HIKM</i>	<i>HI[2]KLN</i>			

If we write the microstates for the spin set d^2 , we get the first 10 microstates in the Table, giving M_L values 3, 2, 1, 0, -1, -2, -3 and 1, 0, -1, corresponding to F and P terms.

Thus the partial terms for two *d* electrons of one spin set are F and P.



Partial Terms Arising from the Occupancy of a Single Spin Set^{a,b}

Orbital set	Orbital occupancy (electrons or holes)							
	0	1	2	3	4	5	6	7
<i>s</i>	S	S						
<i>p</i>	S	P	P	S				
<i>d</i>	S	D	PF	PF	D	S		
<i>f</i>	S	F	PFH	SDFGI	SDFGI	PFH	F	S
<i>g</i>	S	G	PFHK	PF[2]G ^c	SD[2]FG[2]	HI[2]KLN		
				HIKM				

If we write the microstates for the spin set d^2 , we get the first 10 microstates in the Table, giving M_L values 3, 2, 1, 0, -1, -2, -3 and 1, 0, -1, corresponding to F and P terms.

Thus the partial terms for two *d* electrons of one spin set are F and P.



$$\begin{array}{lll} d_{\alpha}^2 d_{\beta}^0 & & (P + F) \times S \rightarrow \begin{cases} P & L = 1 \\ F & L = 3 \end{cases} \quad M_S = +1 \\ 5 \times \frac{4}{2} \times 1 = 10 \quad (\text{degeneracy}) & & \\ \\ d_{\alpha}^0 d_{\beta}^2 & 10 \quad (\text{degeneracy}) \quad S \times (P + F) \rightarrow \begin{cases} P & L = 1 \\ F & L = 3 \end{cases} \quad M_S = -1 \\ & & \\ d_{\alpha}^1 d_{\beta}^1 & & D \times D \quad \rightarrow \begin{cases} G & L = 4 \quad (2+2) \\ F & L = 3 \\ D & L = 2 \quad M_S = 0 \\ P & L = 1 \\ S & L = 0 \quad (2-2) \end{cases} \\ 5 \times 5 = 25 \quad (\text{degeneracy}) & & \end{array}$$



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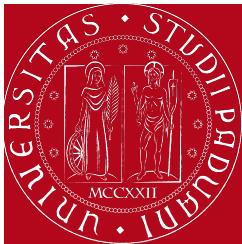
$m_l = +2$	$+1$	0	-1	-2	$M_L = \sum m_l$	$M_S = \sum m_s$
/	/				3	+1,0,0,-
/		/			2	+1,0,0,-
/			/		1	+1,0,0,-
/				/	0	+1,0,0,-
/	/				1	+1,0,0,-
/		/			0	+1,0,0,-
/			/		-1	+1,0,0,-
/	/				-1	+1,0,0,-
/			/		-2	+1,0,0,-
		/	/		-3	+1,0,0,-
x					4	0
x					2	0
x					0	0
x					-2	0
x					-4	0

Array for d

	4	1
	3	1 2
	2	1 3
	1	2 4
M_L	0	2 5
	-1	2 4
	-2	1 3
	-3	1 2
	-4	1
M_S	1	0
		M_S

Arrays for spectral terms contained in array for d

$$\begin{array}{c|c}
 4 & 1 \\
 3 & 1 \\
 2 & 1 \\
 1 & 1 \\
 \hline
 M_L & 0 \quad L = 4 \\
 & 1 \quad S = 0 \\
 & 1 \quad \text{term } {}^1G \\
 -1 & 1 \\
 -2 & 1 \\
 -3 & 1 \\
 -4 & 1 \\
 \hline
 0 & M_S
 \end{array}
 \quad
 \begin{array}{c|ccc}
 3 & 1 & 1 & 1 \\
 2 & 1 & 1 & 1 \\
 1 & 1 & 1 & 1 \\
 \hline
 M_L & 0 & 1 & 1 \\
 & 1 & 1 & 1 \\
 & 1 & 1 & 1 \\
 -1 & 1 & 1 & 1 \\
 -2 & 1 & 1 & 1 \\
 -3 & 1 & 1 & 1 \\
 \hline
 1 & 0 & -1 & \\
 & & M_S & L = 3 \\
 & & & S = 1 \\
 & & & \text{term } {}^3A
 \end{array}$$



$$d^3 \rightarrow \frac{[2\ell(\ell+1)]!}{n![2\ell(\ell+1)-n]!} = \frac{10!}{3!7!} = \frac{10 \times 9 \times 8}{2 \times 3} = 120$$

$$\underbrace{d_{\alpha}^3}_{5 \times \frac{4}{2}} = 10$$

$$\underbrace{d_{\beta}^3}_{5 \times \frac{4}{2}} = 10$$

$$\underbrace{d_{\alpha}^2}_{5 \times \frac{4}{2}} \underbrace{d_{\beta}^1}_{5 \times \frac{4}{2}} = 10 \times 5 = 50$$

$$\underbrace{d_{\alpha}^1}_{5 \times \frac{4}{2}} \underbrace{d_{\beta}^2}_{5 \times \frac{4}{2}} = 5 \times 10 = 50$$

$$d_{\alpha}^3 d_{\beta}^0 \left(\text{or } d_{\alpha}^0 d_{\beta}^3 \right) \rightarrow {}^4 \left[(P+F) \times S \right] = {}^4P + {}^4F$$

$$M_s = \pm \frac{3}{2} \quad \text{Degeneracy} = 4 \times 3 + 4 \times 7 = 40; \quad M_S = \pm \frac{1}{2} \text{ taken into account}$$

$$d_{\alpha}^2 d_{\beta}^1 \left(\text{or } d_{\alpha}^1 d_{\beta}^2 \right) \rightarrow {}^2 \left[(P+F) \times D \right] \quad M_s = \pm \frac{1}{2} \quad \begin{aligned} P \times D &= \textcolor{red}{F} + D + \textcolor{blue}{P} & (2+1 \leq L \leq 2-1) \\ F \times D &= H + G + F + D + P & (3+2 \leq L \leq 3-2) \end{aligned}$$

$$d^3 \rightarrow \underbrace{{}^4F_{28} + {}^4P_{12} + {}^2H_{22} + {}^2G_{18} + {}^2F_{14} + 2 {}^2D_{20} + {}^2P_6}_{120}$$



Allowed terms for *p* and *d* configuration

	<i>Singlets</i>	<i>Douplets</i>	<i>Triplets</i>	<i>Quartets</i>	<i>Quintets</i>	<i>Sextets</i>
p, p^5	–	<i>P</i>	–	–	–	–
p^2, p^4	<i>SD</i>	–	<i>P</i>	–	–	–
p^3	–	<i>PD</i>	–	<i>S</i>	–	–
d, d^9	–	<i>D</i>	–	–	–	–
d^2, d^8	<i>SDG</i>	–	<i>PF</i>	–	–	–
d^3, d^7	–	<i>PDDFGH</i>	–	<i>PF</i>	–	–
d^4, d^6	<i>SSDDFGGI</i>	–	<i>PPDFFGH</i>	–	<i>D</i>	–
d^5	–	<i>SPDDDFGGHI</i>	–	<i>PDFG</i>	–	<i>S</i>

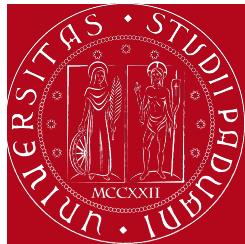


Partial Terms Arising from the Occupancy of a Single Spin Set^{a,b}

Orbital set	Orbital occupancy (electrons or holes)							
	0	1	2	3	4	5	6	7
<i>s</i>	S	S						
<i>p</i>	S	P	P	S				
<i>d</i>	S	D	PF	PF	D	S		
<i>f</i>	S	F	PFH	SDFGI	SDFGI	PFH	F	S
<i>g</i>	S	G	PFHK	PF[2]G ^c HIKM	SD[2]FG[2] HI[2]KLN			

If we write the microstates for the spin set d^2 , we get the first 10 microstates in the Table, giving M_L values 3, 2, 1, 0, -1, -2, -3 and 1, 0, -1, corresponding to F and P terms.

Thus the partial terms for two *d* electrons of one spin set are F and P.



		M_S			
		+3/2	+1/2	-1/2	-3/2
M_L	8			2	
	7				4
	6				10
	5				14
	4				22
	3				30
	2				38
	1				40
	0				44
	-1				40
	-2				38
	-3				30
	-4				22
	-5				14
	-6				10
	-7				4
	-8				2
Total microstates		35	147	147	35
					364



SOLUTION For f^3 , there are $14 \times \frac{13}{2} \times \frac{12}{3} = 364$ microstates. The possible configurations are as follows.

$$f_{\alpha}^3 \quad f_{\beta}^3 \quad f_{\alpha}^2 f_{\beta}^1 \quad f_{\alpha}^1 f_{\beta}^2$$

Degeneracy 35 35 $21 \times 7 = 147$ $7 \times 21 = 147$ Total = 364

$$f_{\alpha}^3 f_{\beta}^0 \quad (\text{or } f_{\alpha}^0 f_{\beta}^3) \quad \text{yields } {}^4[S(S+D+F+G+I)] = {}^4S + {}^4D + {}^4F + {}^4G + {}^4I$$

$$M_S = \pm \frac{3}{2} \quad \text{Degeneracy} = 140 = 4 + 20 + 28 + 36 + 52$$

The degeneracy here is 140 (not 70) because the $M_S = \pm \frac{1}{2}$ terms are included. We must drop the corresponding doublets generated below.

$$f_{\alpha}^2 f_{\beta}^1 \quad (\text{or } f_{\alpha}^1 f_{\beta}^2) \quad \text{yields } {}^2[F(P+F+H)] \quad M_S = \pm \frac{1}{2}.$$

Drop 2S , 2D , 2F , 2G , 2I ,

$$F \times P = D + F + G \quad (3-1 \text{ to } 3+1),$$

$$F \times F = S + P + D + K + G + H + I,$$

$$F \times H = D + F + G + H + I + K + L.$$

The remaining terms are

$${}^2P, {}^2D[2], {}^2F[2], {}^2G[2], {}^2H[2], {}^2I, {}^2K, {}^2L, {}^4S, {}^4D, {}^4F, {}^4G, {}^4I.$$

Ground-state term is 4I ($L = 6, S = \frac{3}{2}, J = \frac{15}{2}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2}$). Ground-state level is ${}^4I_{9/2}$.



Table 1. Partial Terms Arising from the Occupancy of a Single Spin Set (either α or β)

Orbital Occupancy (electrons or holes)	0	1	2	3	4
<i>Orbital Set</i>					
<i>s</i>	<i>S</i> (1)	<i>S</i> (1)			
<i>p</i>	<i>S</i> (1)	<i>P</i> (3)			
<i>d</i>	<i>S</i> (1)	<i>D</i> (5)	<i>PF</i> (10)		
<i>f</i>	<i>S</i> (1)	<i>F</i> (7)	<i>PFH</i> (21)	<i>SDF</i> <i>GI</i> (35)	
<i>g</i>	<i>S</i> (1)	<i>G</i> (9)	<i>PFHK</i> (36)	<i>PF</i> [2] <i>G</i> <i>HIK</i> <i>M</i>	<i>SD</i> [2] <i>FG</i> [2] <i>HI</i> [2] <i>KL</i> <i>N</i> (84) (126)

The orbital degeneracy is given in parenthesis; the number of partial terms, in square brackets.