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.

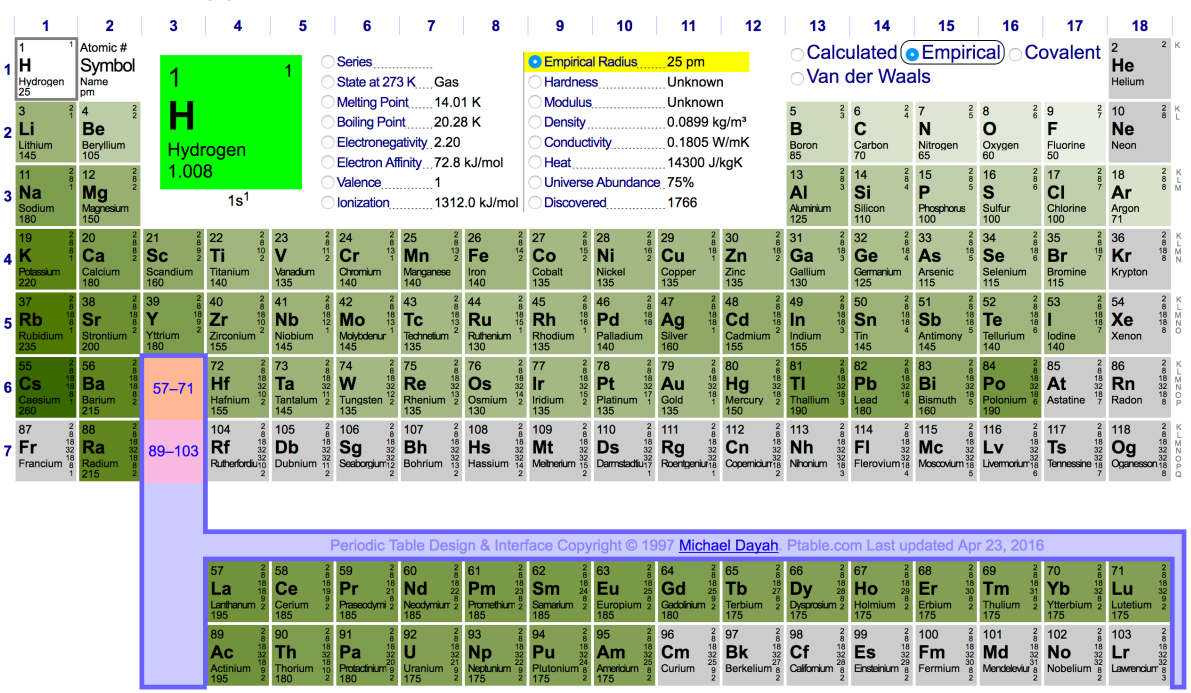
i) The hydroxides tend to be slightly soluble in water giving alkaline solutions, the carbonates tend to be insoluble and so on (**bastnaesite** is a Ln fluorocarbonate $M^{III}CO_3F$).

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-memoire*; it can be exploited.

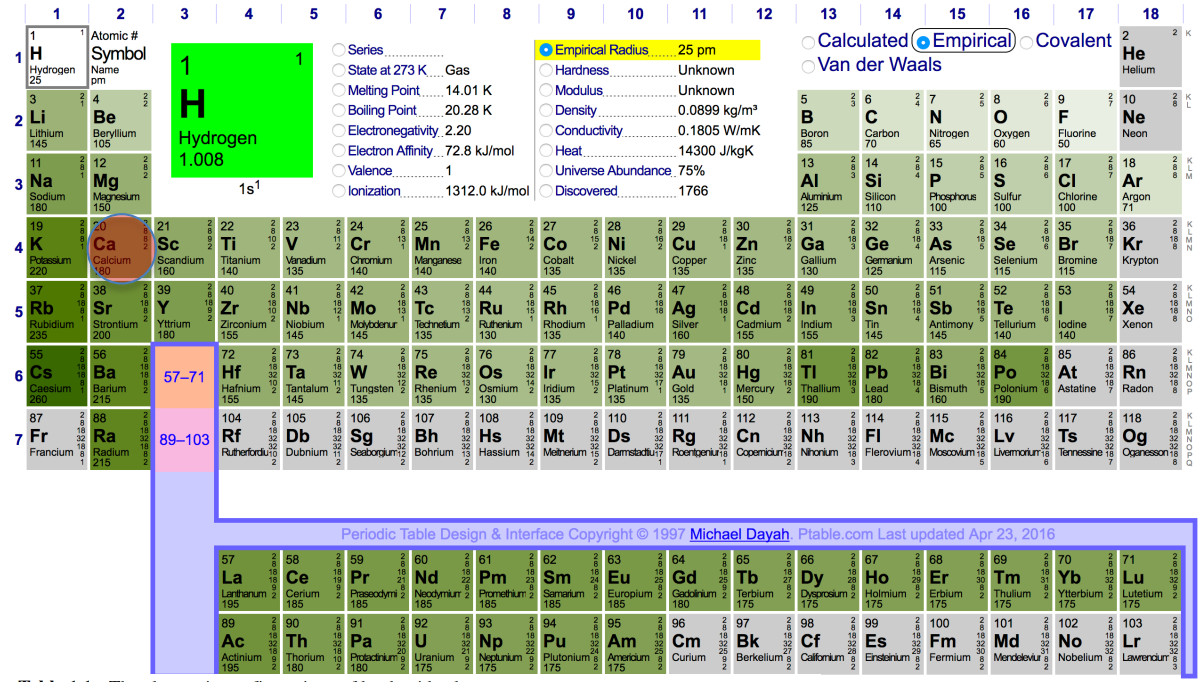
Ca(II) ions are biologically very important - their movement is involved in nerve action, for example. The study of Ca(II) ions is very difficult because they lack any convenient spectroscopic property - a spectroscopic "handle" - by which they can be studied.

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.



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+



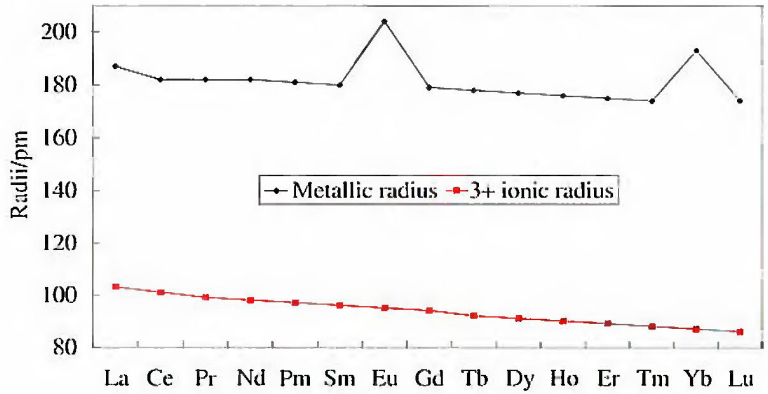
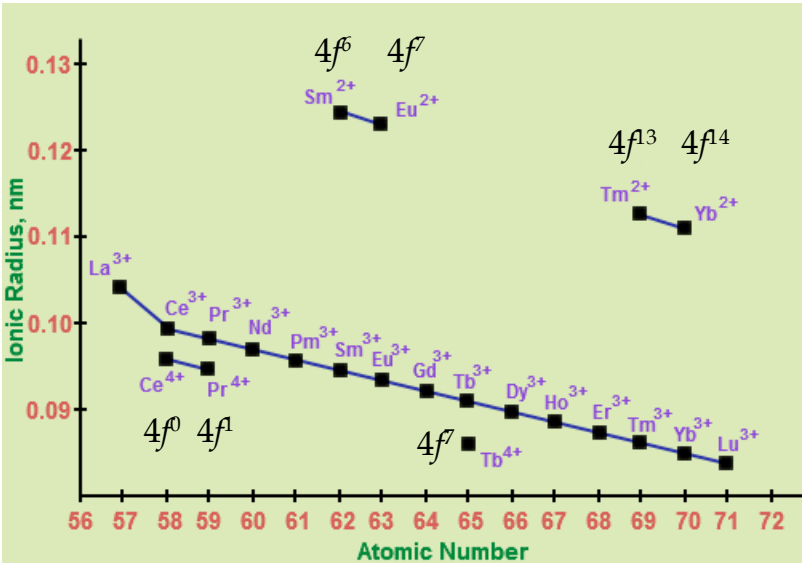


Table 1.1 The electronic configurations of lanthanide elements.

Z	Element		Electronic configurations of neutral atoms 4f	5s	5p	5d	6s	Electronic configurations of trivalent ions	Atomic radius (pm) (coordination number = 12)	Atomic weight
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
			3d	4s	4p	4d	5s			
21	Sc	Inner 18 electrons	1	2				[Ar]	164.06	44.956
39	Y		10	2	6	1	2	[Kr]	180.12	88.906



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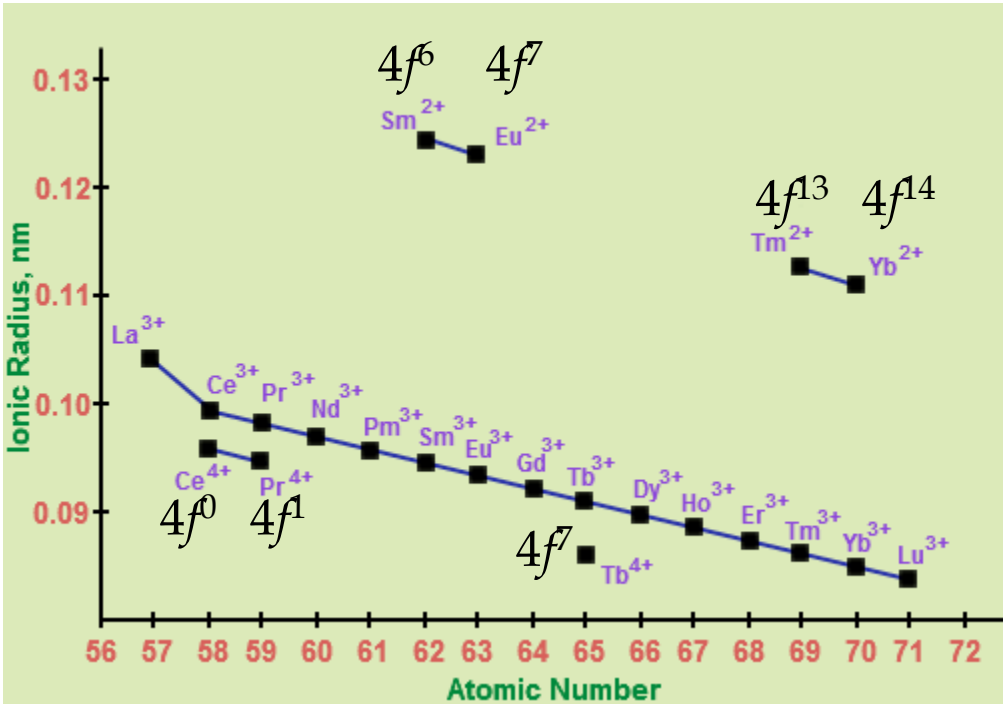

For many years, the lanthanides did not generate much interest, as it was believed that their chemistry was limited, owing to the restricted availability of oxidation states other than that of Ln^{3+}. Eu^{2+}, Yb^{2+}, Sm^{2+}, and Ce^{4+} were the only non-trivalent Ln ions thought achievable in molecular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

$$Ln^{3+} + 1e^- \leftrightarrows Ln^{2+}$$

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)

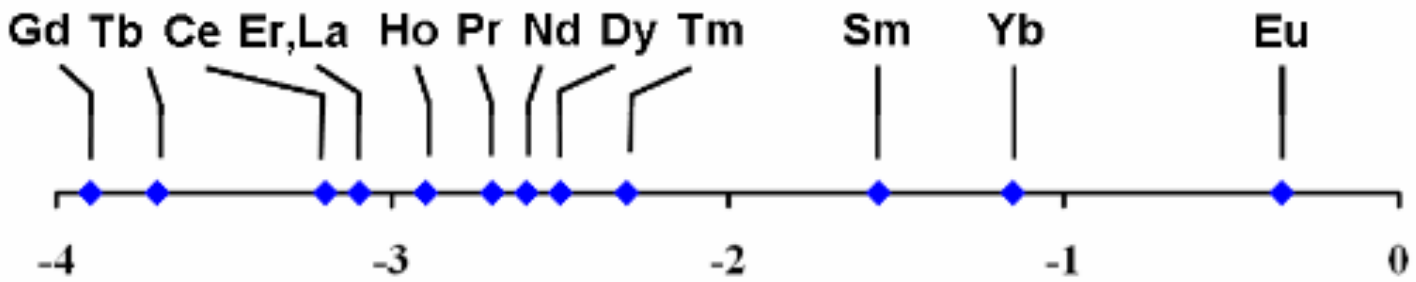

Figure 1. Reduction potentials for the $Ln^{3+} + e^- \rightarrow Ln^{2+}$ process.

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
$Ln^{3+} + 3e \rightarrow Ln$	−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
$Ln^{3+} + e \rightarrow Ln^{2+}$	(−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		
$Ln^{4+} + e \rightarrow Ln^{3+}$		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.

$ClO_4^- + 8\,H^+ + 8e^- \leftrightarrows Cl^- + 4H_2O$ $E^0 = 1.389$ V

$MnO_4^- + 8\,H^+ + 5e^- \leftrightarrows Mn^{2+} + 4H_2O$ $E^0 = 1.507$ V

$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrows 2Cr^{3+} + 7H_2O$ $E^0 = 1.232$ V

$F_2 + 2H^+ + 2e^- \leftrightarrows 2HF$ $E^0 = 3.053$ V

$Li^+ + e^- \leftrightarrows Li$ $E^0 = -3.04$ V

$Na^+ + e^- \leftrightarrows Na$ $E^0 = -2.71$ V

$K^+ + e^- \leftrightarrows K$ $E^0 = -2.93$ V

$Rb^+ + e^- \leftrightarrows Rb$ $E^0 = -2.98$ V

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	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$Ln^{3+} + 3e \rightarrow Ln$	−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
$Ln^{3+} + e \rightarrow Ln^{2+}$	(−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		
$Ln^{4+} + e \rightarrow Ln^{3+}$		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)	

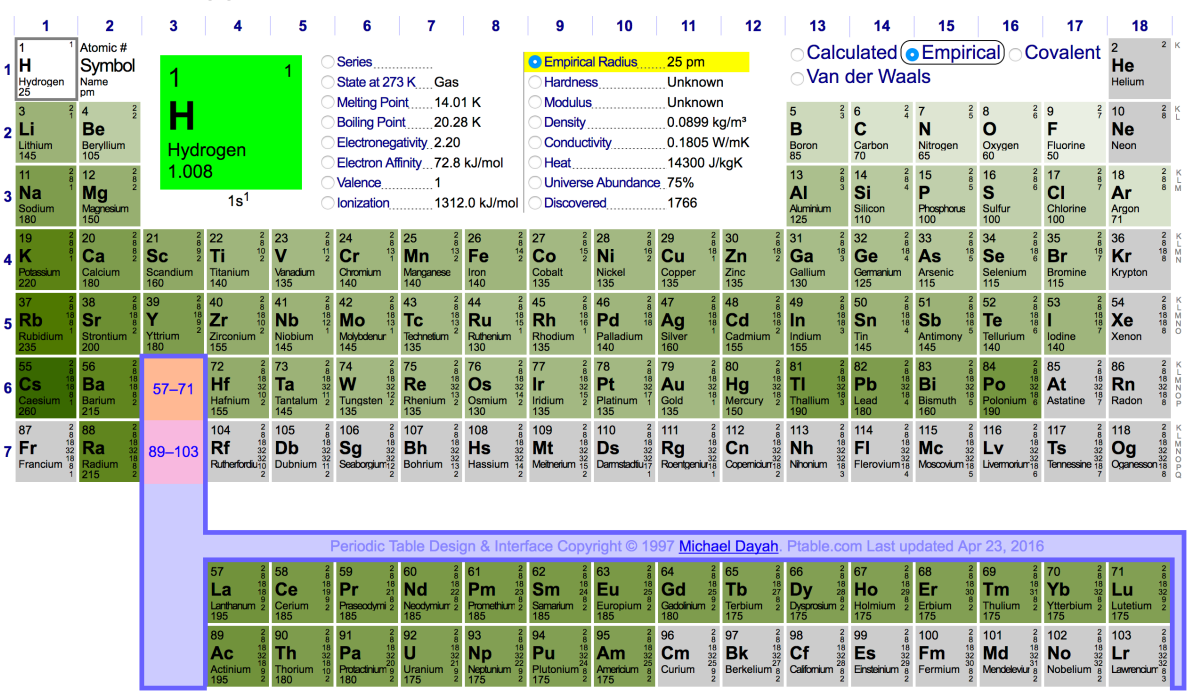
[a] Values in parentheses are estimated.
[b] = in THF.

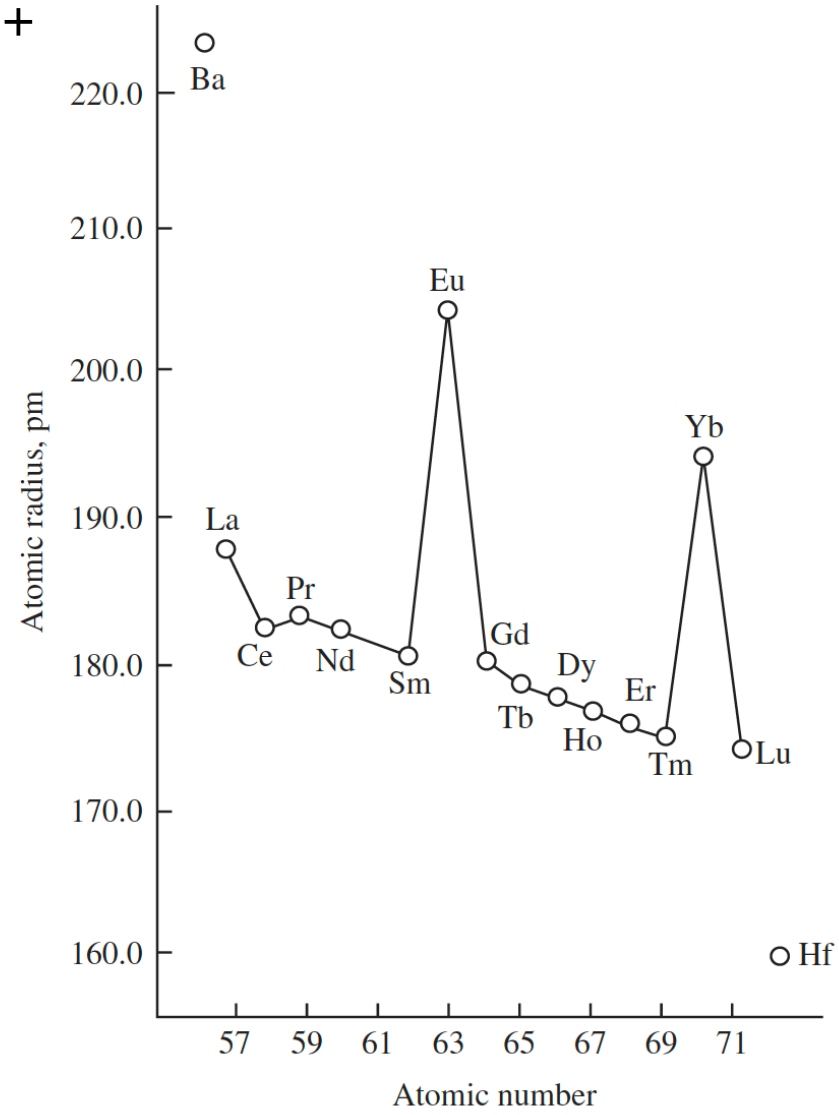
Synproportionation	Ln	+ 2 LnI_3	⟶	3 LnI_2
Synthesis from Pure Elements	Ln	+ I_2	⟶	LnI_2
Reduction of Ln^{3+}		R_nLnX_m	⟶	R_2Ln

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

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+





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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

No radial nodes

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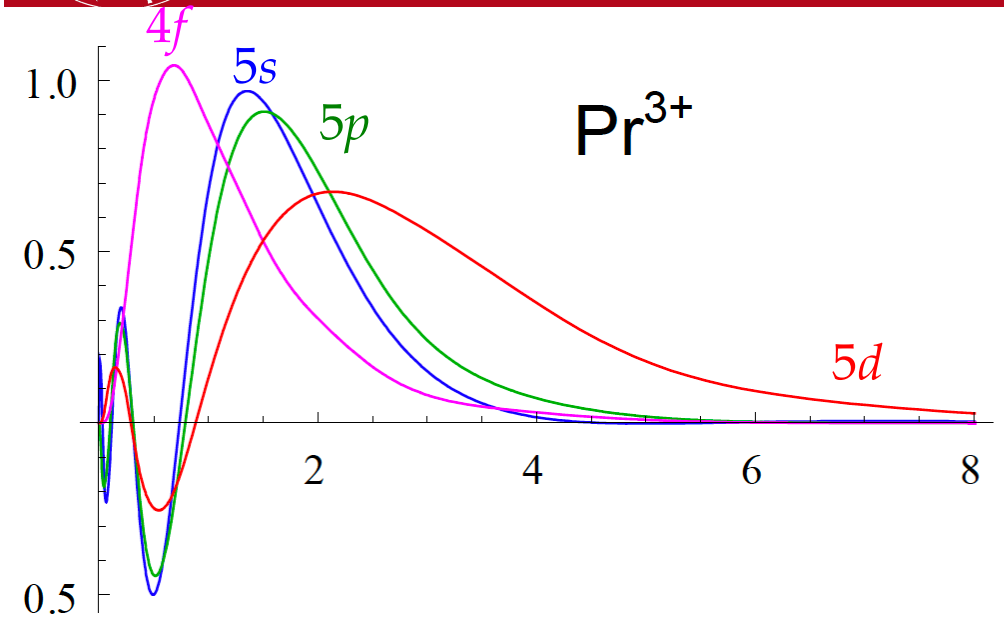

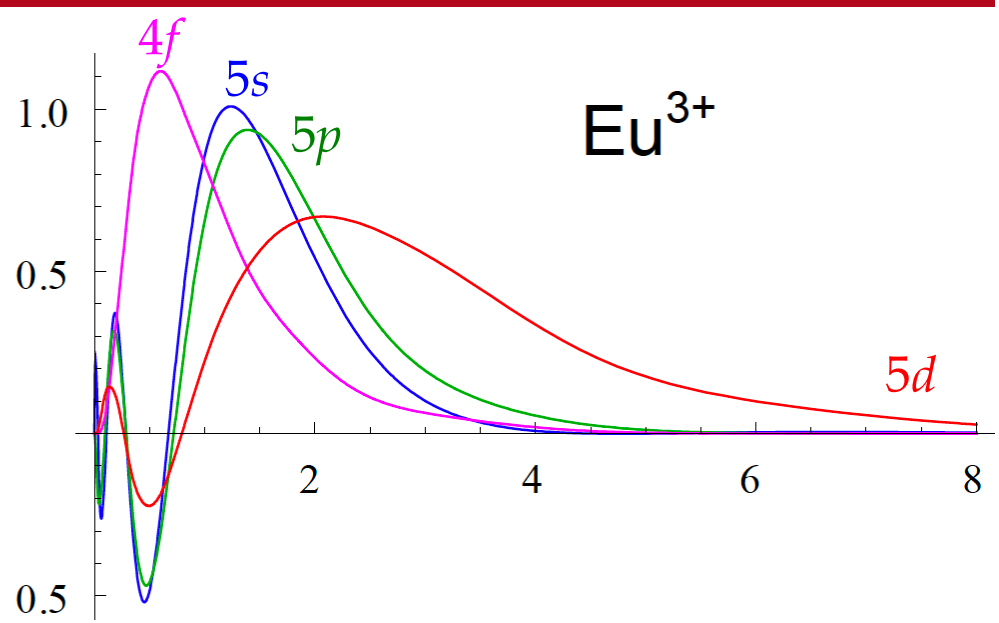

Plots of the radial functions ***rR(r)*** vs *r* (in a.u.) for Pr(III) and Eu(III). Pink, blue, green and red lines correspond to 4*f*, 5*s*, 5*p* and 5*d*.

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

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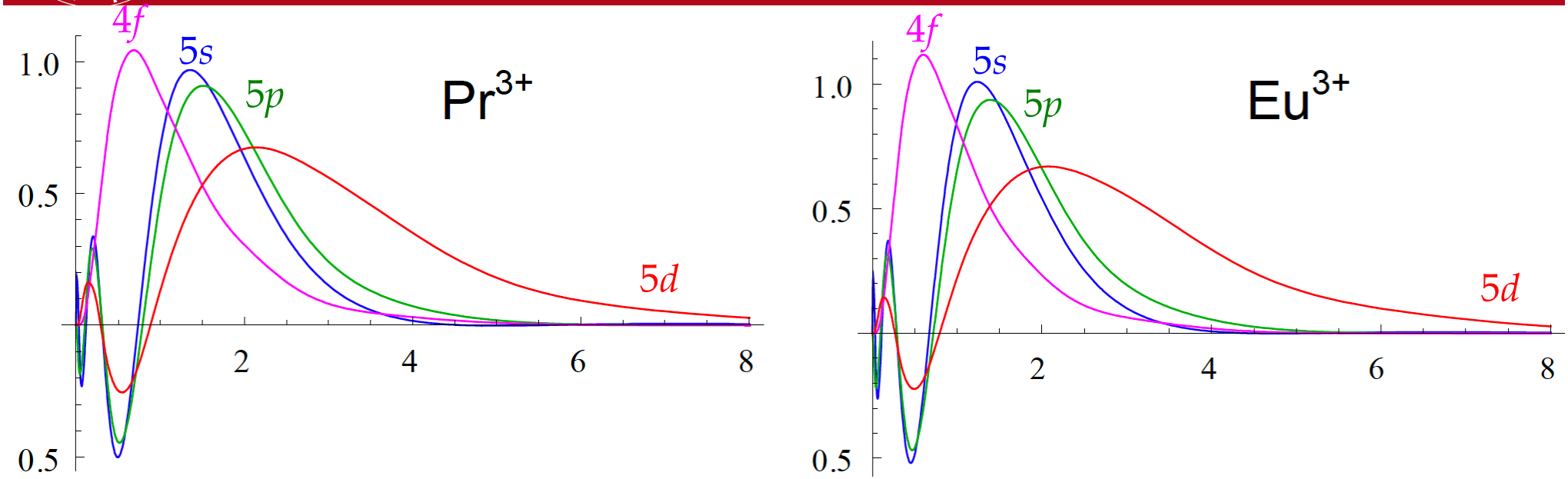

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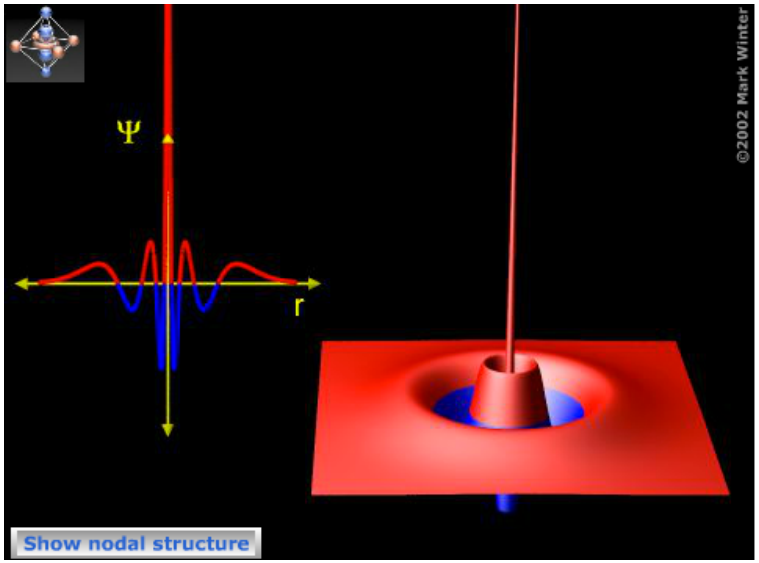

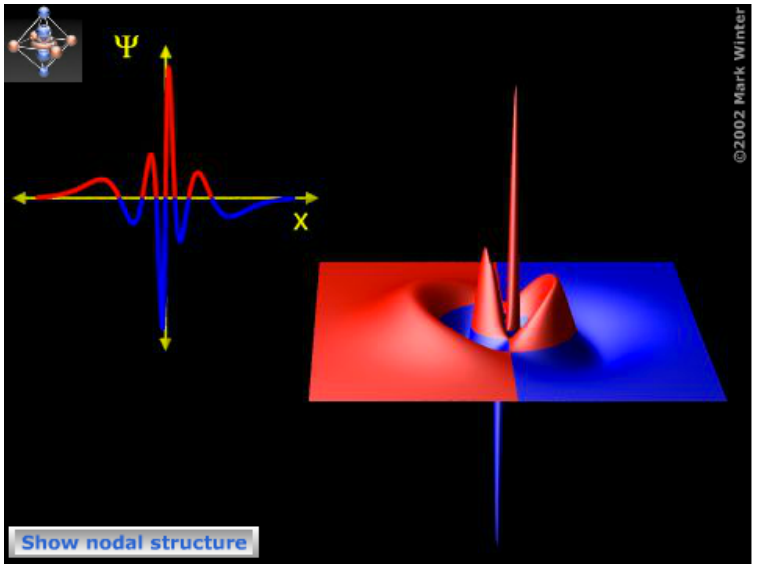

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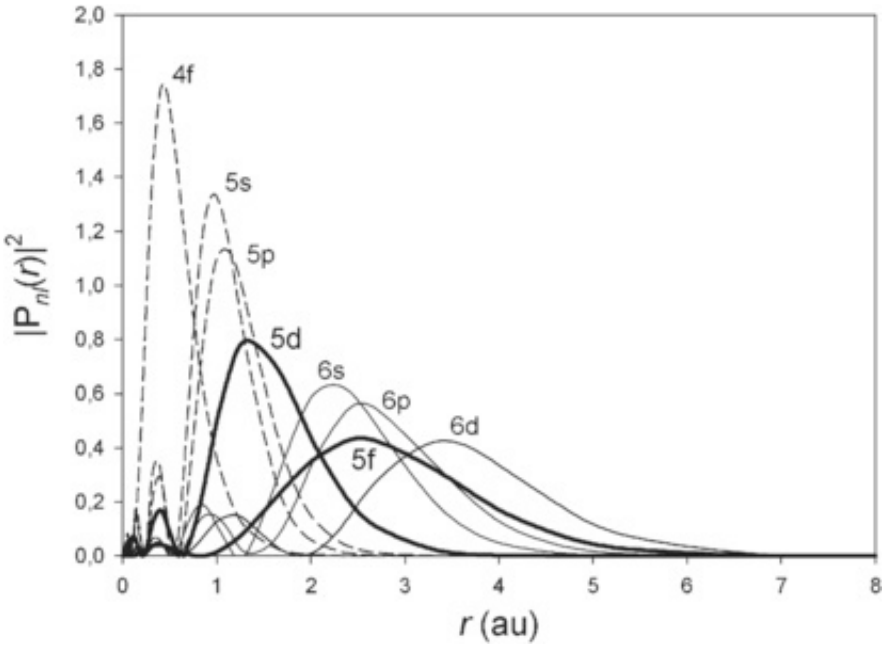
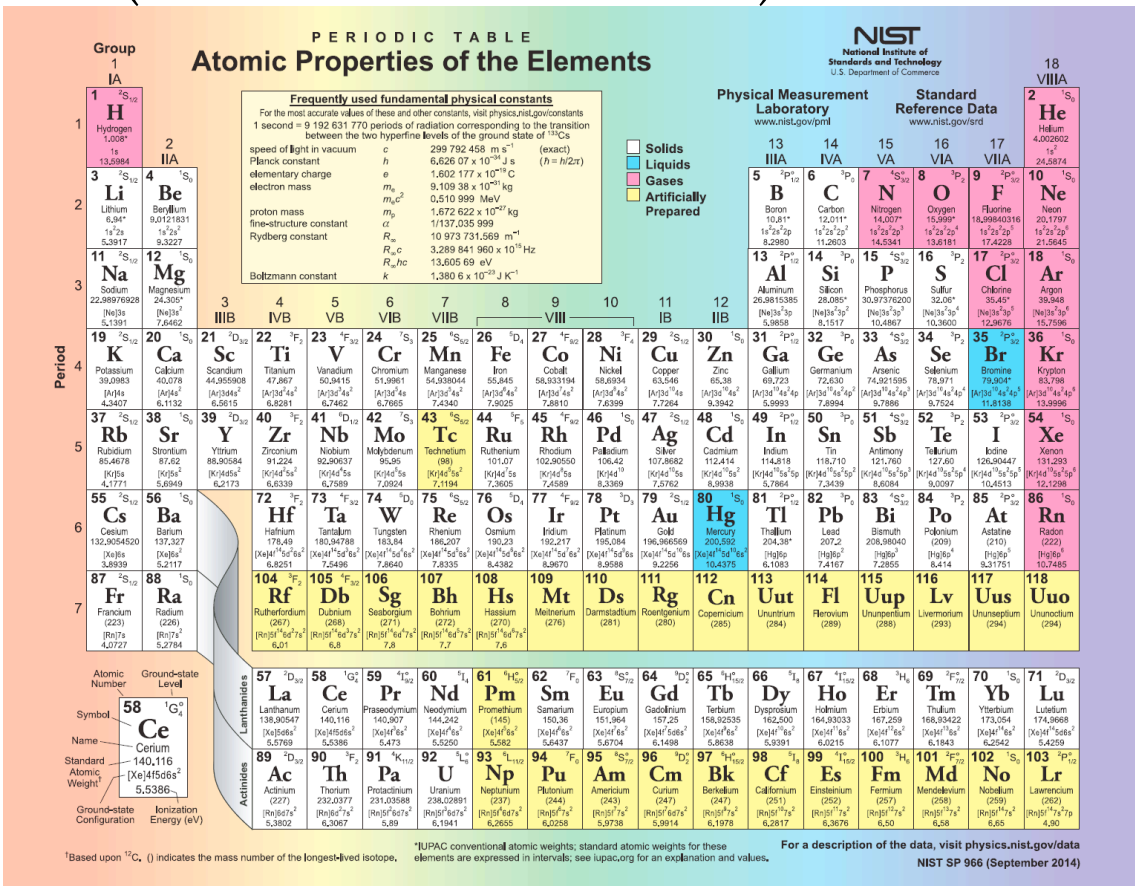
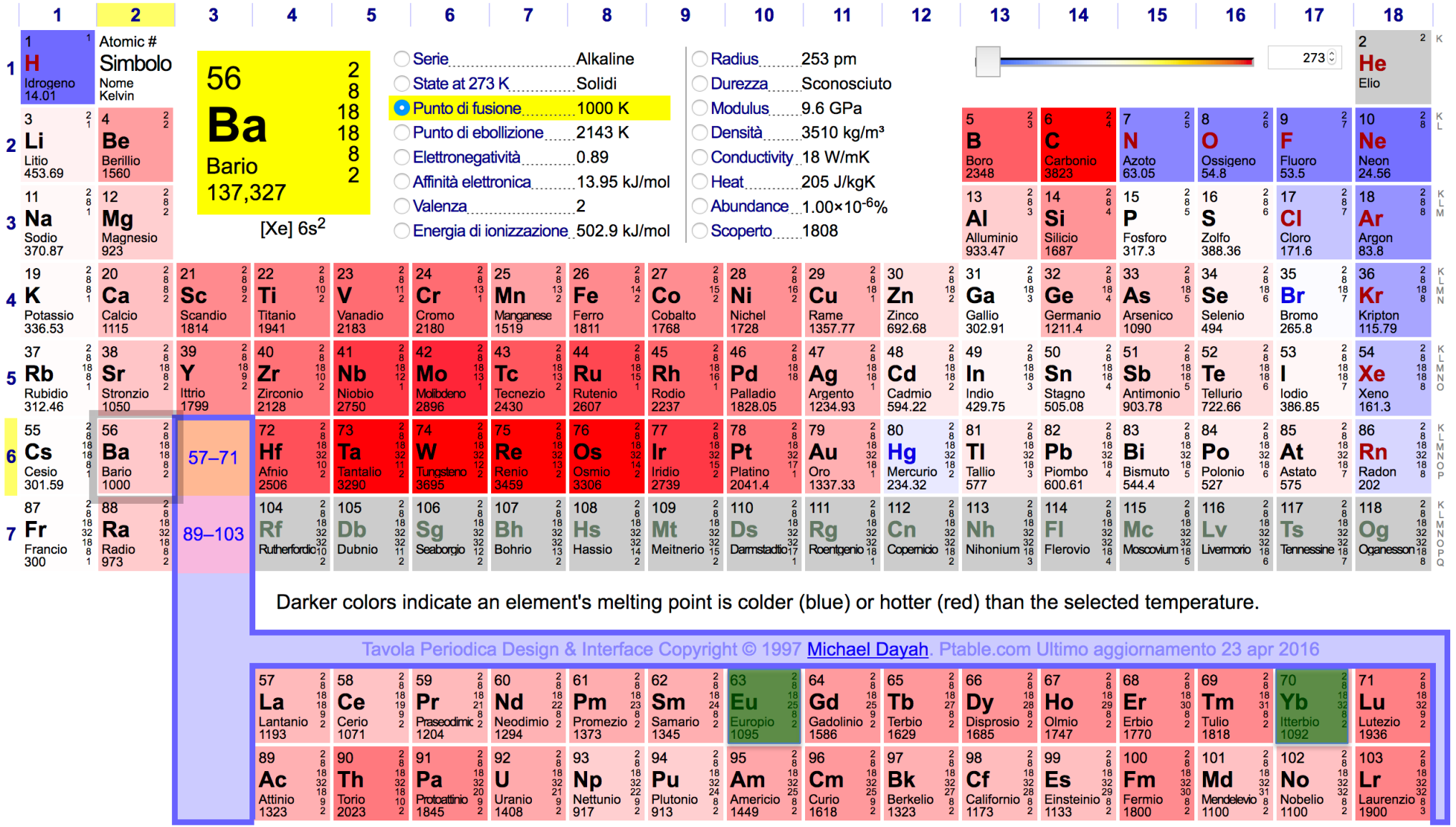


Radial probability functions for hydrogen-like orbitals. Although the 4*f* AOs have their maximum closer to the nucleus than 5*d* and 6*s*, close to the nucleus the density of the latter two both exceed that of the 4*f*.



4*f* 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 5*d* and 6*s* 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 4*f*.

- Silvery white metals with high melting and boiling points



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

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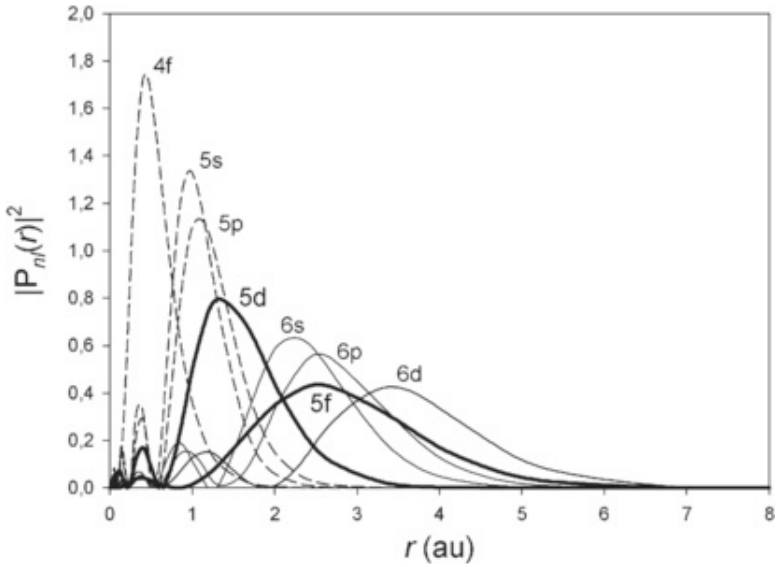
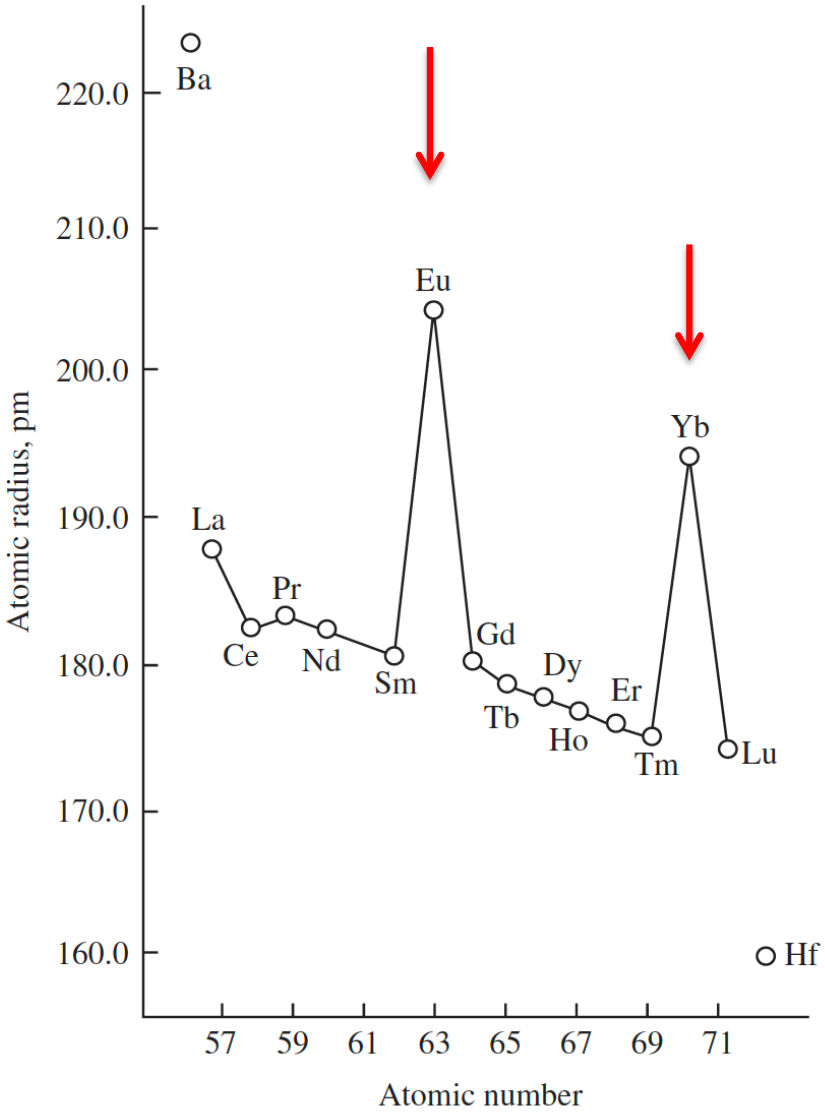
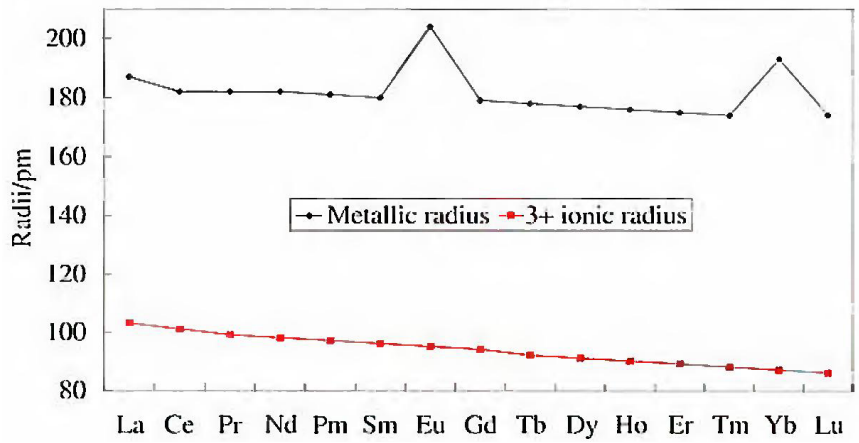
57	La	The inner	0	2	6	1	2	$[Xe]4f^0$	187.91	138.91
58	Ce	orbitals	1	2	6	1	2	$[Xe]4f^1$	182.47	140.12
59	Pr	have been	3	2	6		2	$[Xe]4f^2$	182.80	140.91
60	Nd	full-filled, 46	4	2	6		2	$[Xe]4f^3$	182.14	144.24
61	Pm	electrons	5	2	6		2	$[Xe]4f^4$	(181.0)	(147)
62	Sm	in all	6	2	6		2	$[Xe]4f^5$	180.41	150.36
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
			3d	4s	4p	4d	5s			
21	Sc	Inner 18 electrons	1	2				[Ar]	164.06	44.956
39	Y		10	2	6	1	2	[Kr]	180.12	88.906

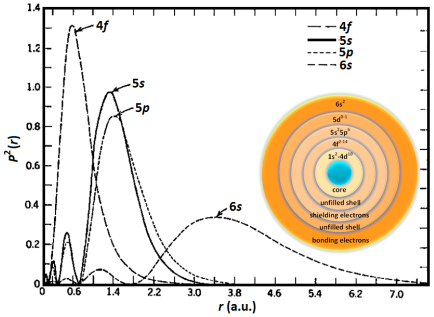


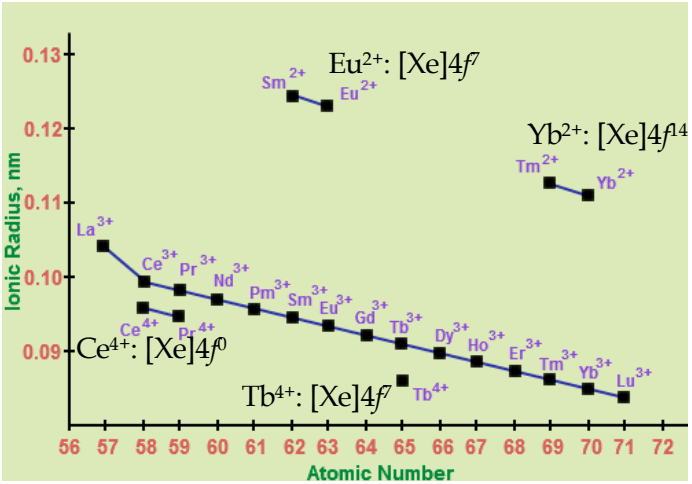


Chemical element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Image															
Density (g/cm^3)	6.162	6.770	6.77	7.01	7.26	7.52	5.244	7.90	8.23	8.540	8.79	9.066	9.32	6.90	9.841
Melting point (°C)	920	795	935	1024	1042	1072	826	1312	1356	1407	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 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 6s^2 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/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
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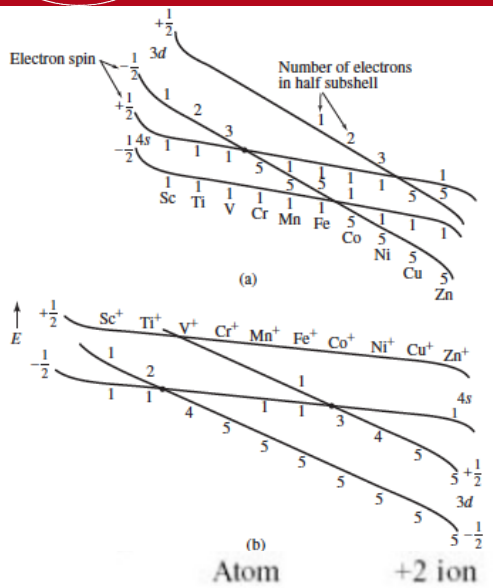
Boiling point (°C)	3464	3443	3520	3074	3000	1794	1529	3273	3230	2567	2720	2868	1950	1196	3402
Atomic electron configuration*	**5d^1**	4f^1**5d^1**	4f^3	4f^4	4f^5	4f^6	4f^7	4f^7**5d^1**	4f^9	4f^{10}	4f^{11}	4f^{12}	4f^{13}	4f^{14}	4f^{14}**5d^1**
Metal lattice (RT)	dhcp	fcc	dhcp	dhcp	dhcp	**	bcc	hcp	hcp	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 6s^2 electronic shells

Eu^{2+}: [Xe]4f^7; Yb^{2+}: [Xe]4f^{14}
Ce^{4+}: [Xe]4f^0; Tb^{4+}: [Xe]4f^7

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	—



	Atom	+2 ion
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	$4s^1 3d^{10}$	$3d^9$

Schematic Energy Levels for Transition Elements.

(a) Schematic interpretation of electron configurations for transition elements in terms of intra-orbital repulsion and trends in subshell energies.

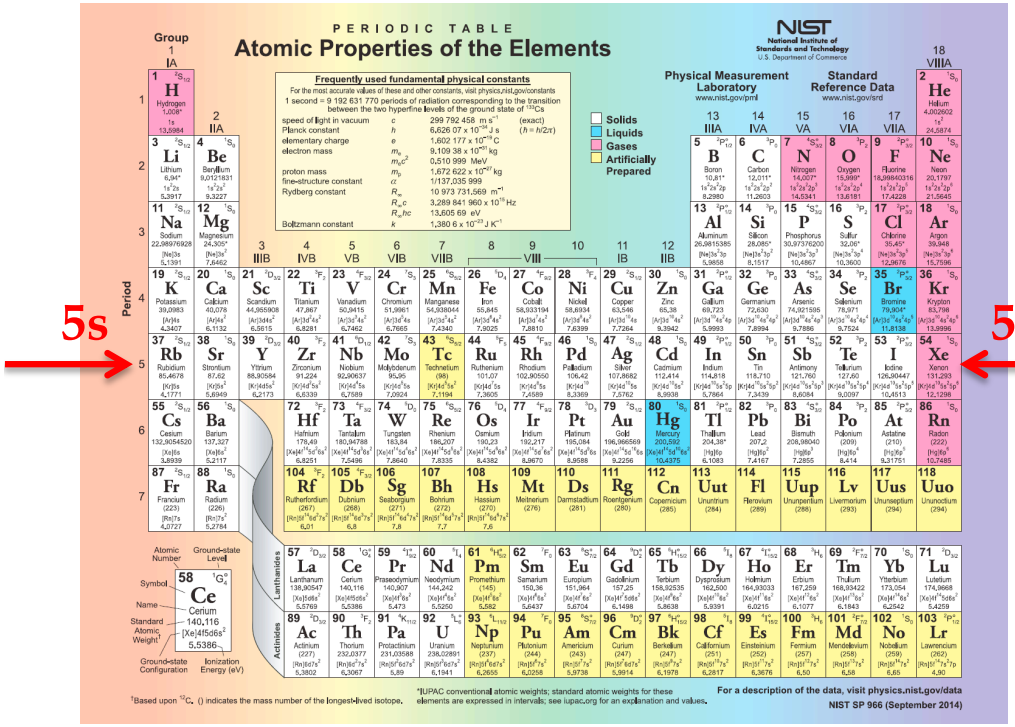
(b) A similar diagram for ions, showing the shift in the crossover points on removal of an electron. The shift is even more pronounced for metal ions having 2+ or greater charges. As a consequence, transition-metal ions with 2+ or greater charges have no *s* electrons, only *d* electrons in their outer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

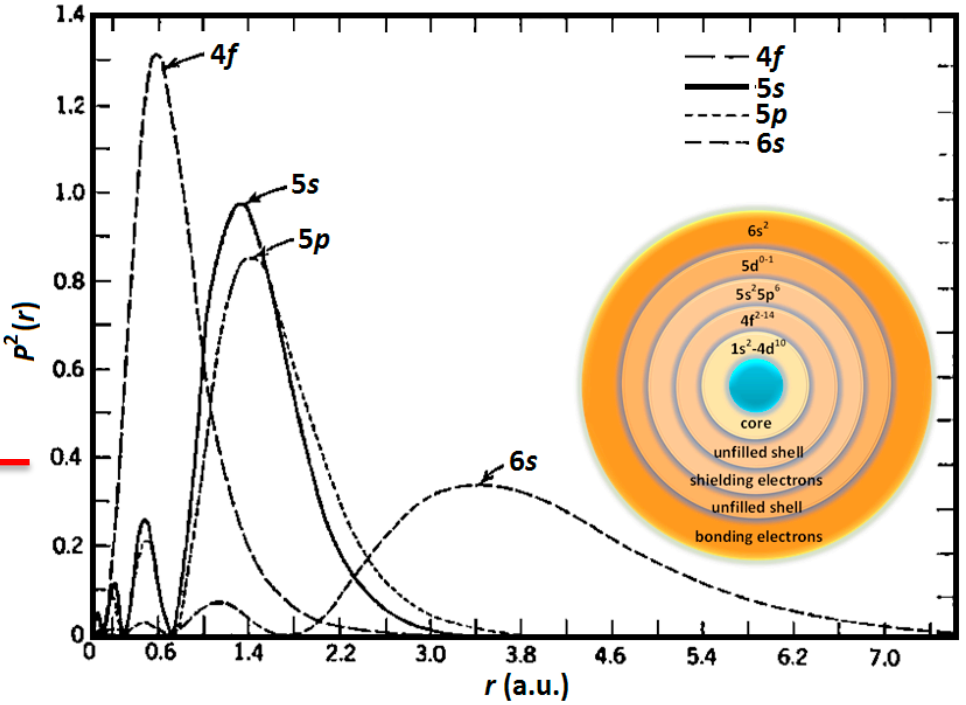
Eu^{2+}: [Xe]$4f^7$; Yb^{2+}: [Xe]$4f^{14}$
Ce^{4+}: [Xe]$4f^0$; Tb^{4+}: [Xe]$4f^7$

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	—

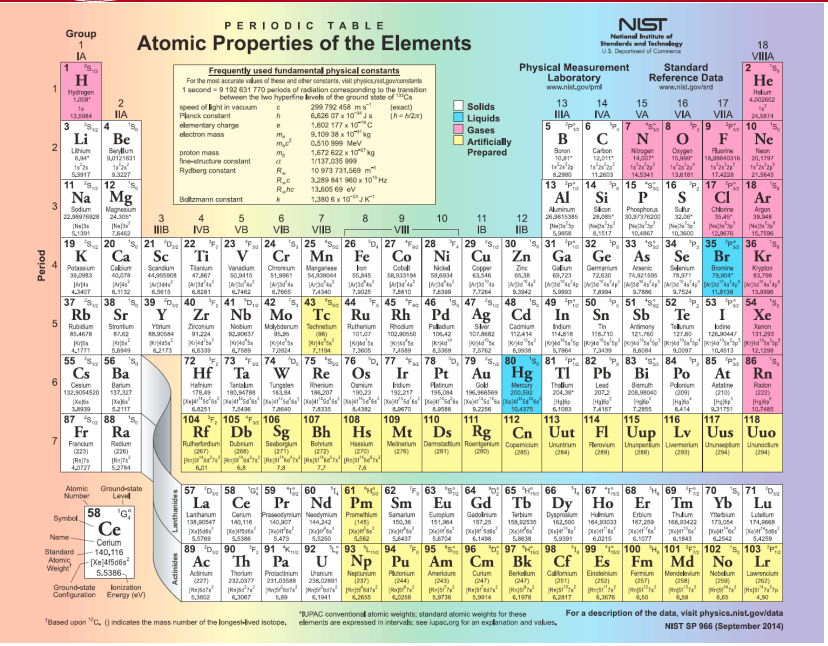
Atomic number	Name	Symbol	Isolated atom electron configuration	M^{3+} f electron configuration
57	Lanthanum	La	$5d^1 6s^2$	$4f^0$
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$
60	Neodymium	Nd	$4f^4 6s^2$	$4f^3$
61	Promethium	Pm	$4f^5 6s^2$	$4f^4$
62	Samarium	Sm	$4f^6 6s^2$	$4f^5$
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	$4f^{14} 5d^1 6s^2$	$4f^{14}$

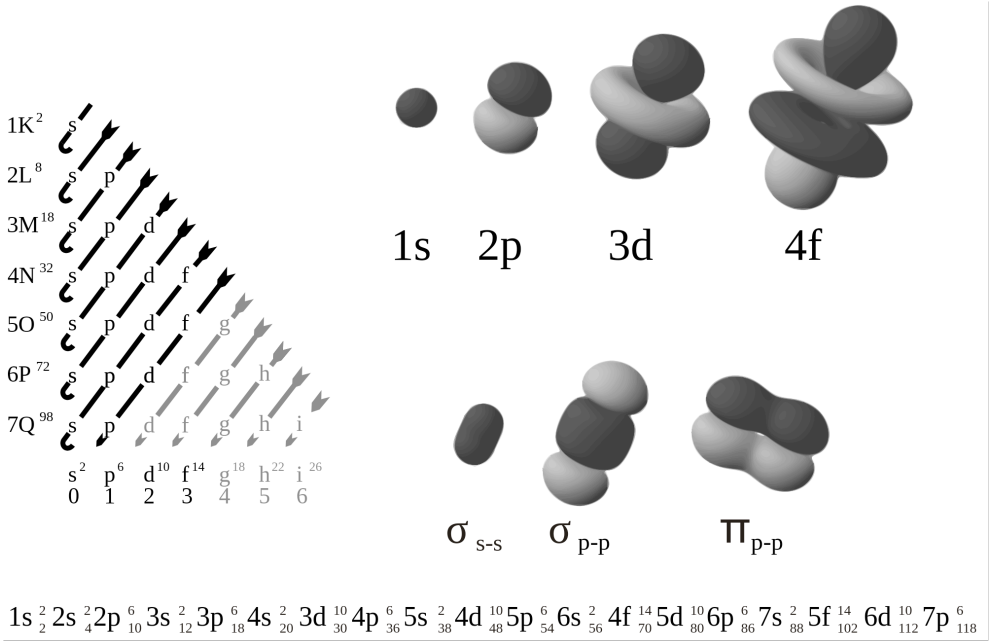
Note: Promethium, effectively, does not occur in nature. It is a fission product of uranium and may be made, for example, by neutron bombardment of neodymium to give an isotope with a half-life of just under 4 years.



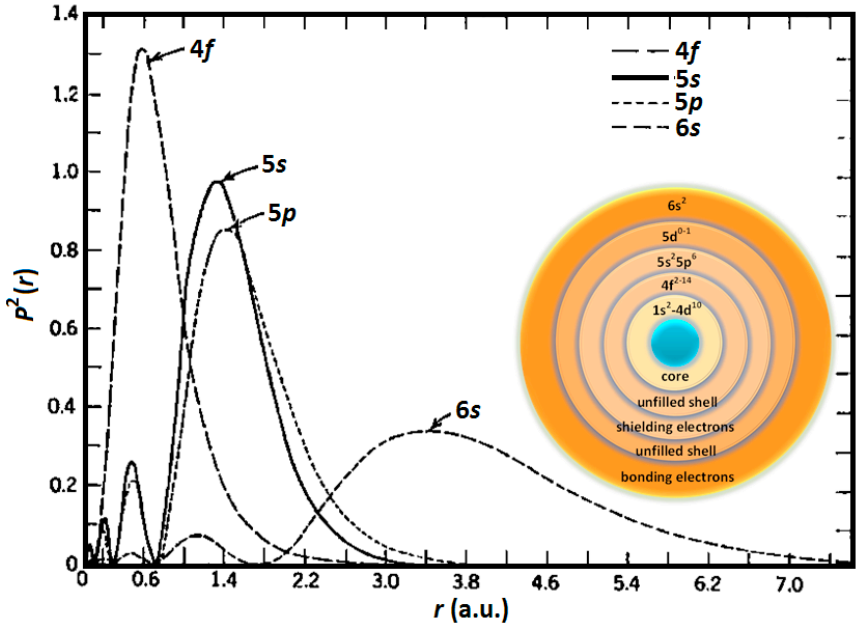


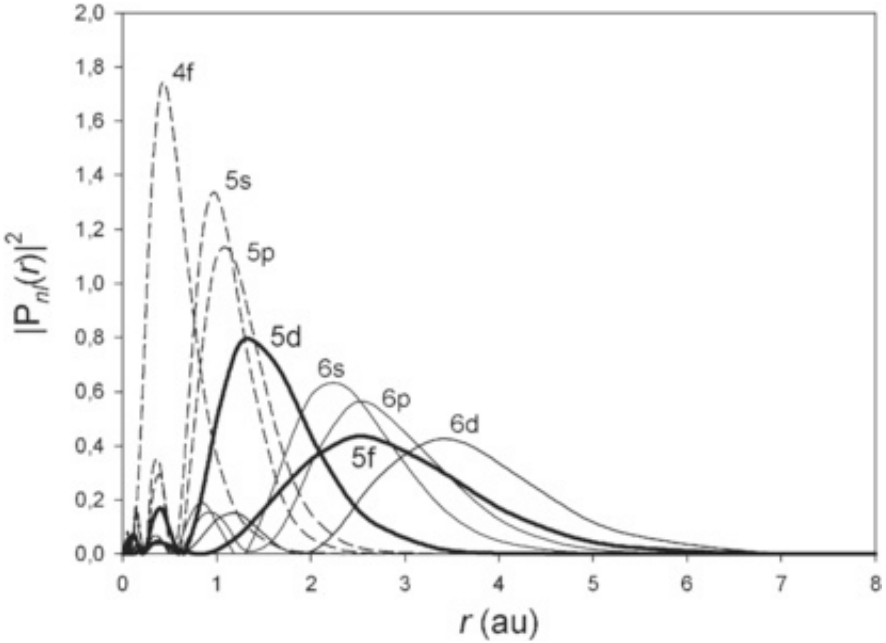
The 4*f* e^- of the lanthanide element ions are shielded from the perturbing effects of ligands by outer lying *s* and *p* e^-. This shielding accounts for the great similarity of the chemical properties of lanthanide compounds, it also explains the evidence that the magnitude of their ligand splitting parameters are **≈ 2** order of magnitude smaller than those of transition series ions and that superhyperfine splitting are not observed in their EPR spectra.

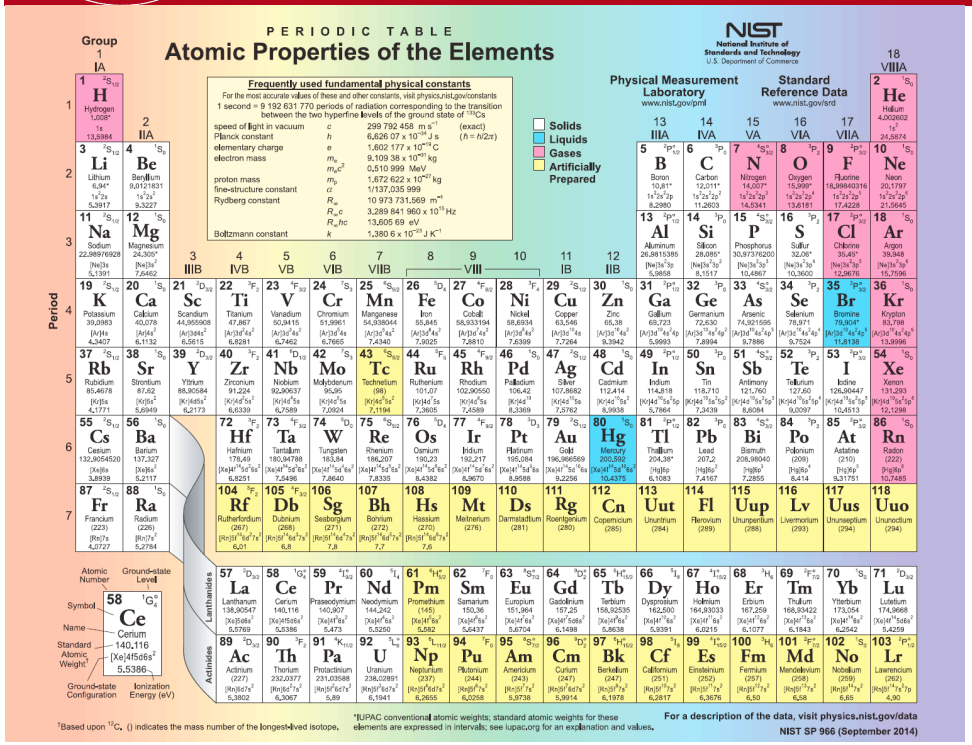


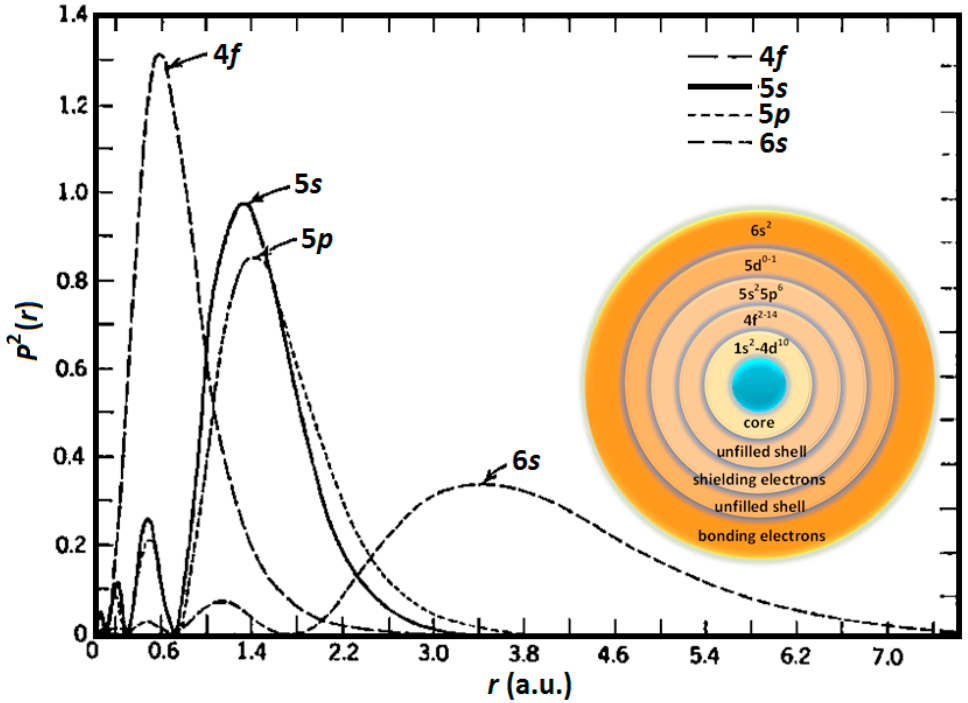


$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ 7s^2\ 5f^{14}\ 6d^{10}\ 7p^6$









$$Y_3^{-3}(\theta,\varphi) = \frac{1}{8}\sqrt{\frac{35}{\pi}} \cdot e^{-3i\varphi} \cdot \sin^3\theta \quad = \frac{1}{8}\sqrt{\frac{35}{\pi}} \cdot \frac{(x-iy)^3}{r^3}$$

$$Y_3^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{105}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2\theta \cdot \cos\theta \quad = \frac{1}{4}\sqrt{\frac{105}{2\pi}} \cdot \frac{(x-iy)^2 z}{r^3}$$

$$Y_3^{-1}(\theta,\varphi) = \frac{1}{8}\sqrt{\frac{21}{\pi}} \cdot e^{-i\varphi} \cdot \sin\theta \cdot (5\cos^2\theta - 1) \quad = \frac{1}{8}\sqrt{\frac{21}{\pi}} \cdot \frac{(x-iy)(4z^2 - x^2 - y^2)}{r^3}$$

$$Y_3^{0}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{7}{\pi}} \cdot (5\cos^3\theta - 3\cos\theta) \quad = \frac{1}{4}\sqrt{\frac{7}{\pi}} \cdot \frac{z(2z^2 - 3x^2 - 3y^2)}{r^3}$$

$$Y_3^{1}(\theta,\varphi) = \frac{-1}{8}\sqrt{\frac{21}{\pi}} \cdot e^{i\varphi} \cdot \sin\theta \cdot (5\cos^2\theta - 1) \quad = \frac{-1}{8}\sqrt{\frac{21}{\pi}} \cdot \frac{(x+iy)(4z^2 - x^2 - y^2)}{r^3}$$

$$Y_3^{2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{105}{2\pi}} \cdot e^{2i\varphi} \cdot \sin^2\theta \cdot \cos\theta \quad = \frac{1}{4}\sqrt{\frac{105}{2\pi}} \cdot \frac{(x+iy)^2 z}{r^3}$$

$$Y_3^{3}(\theta,\varphi) = \frac{-1}{8}\sqrt{\frac{35}{\pi}} \cdot e^{3i\varphi} \cdot \sin^3\theta \quad = \frac{-1}{8}\sqrt{\frac{35}{\pi}} \cdot \frac{(x+iy)^3}{r^3}$$

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

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

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

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

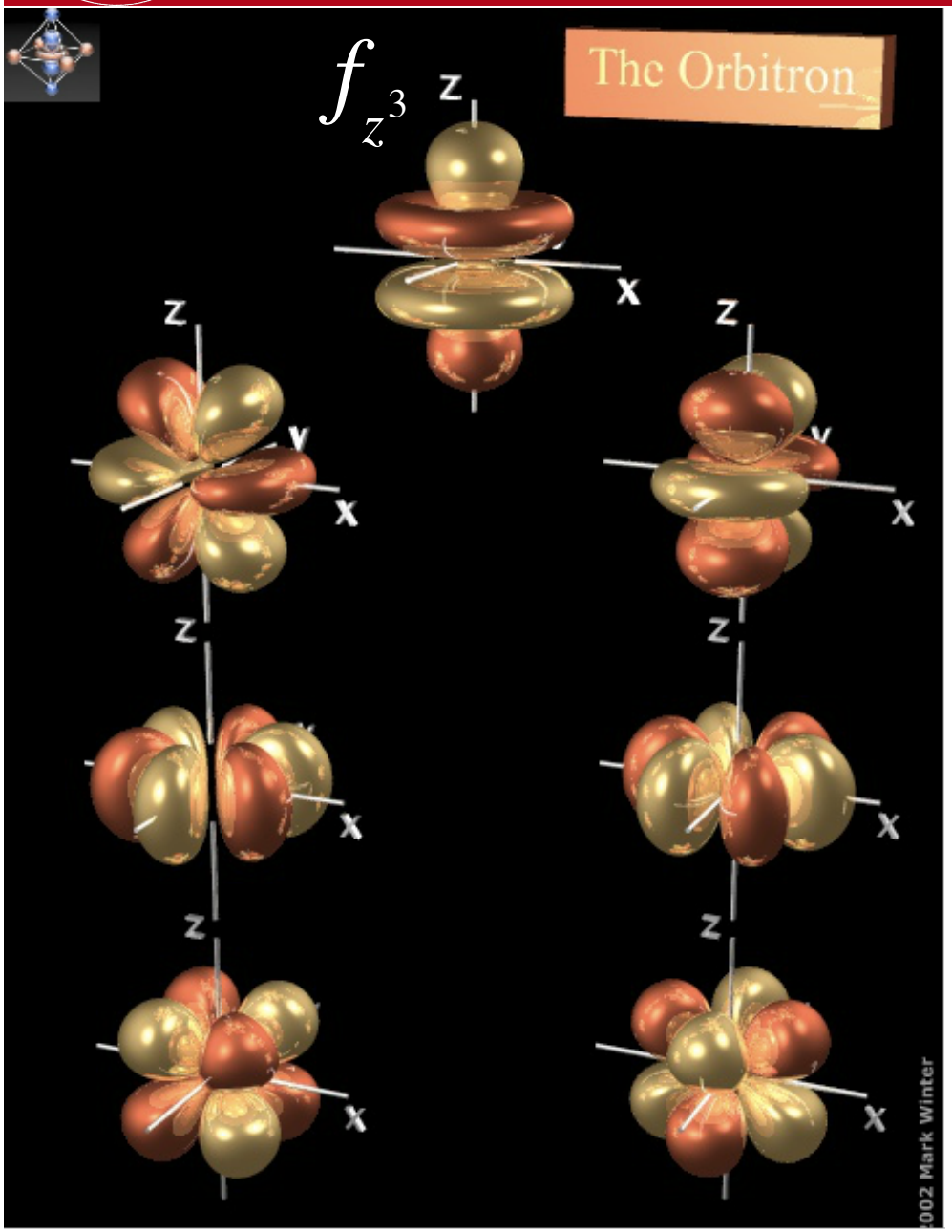
$$Y_{31} = f_{xz^2} = \sqrt{\frac{1}{2}}\left(Y_3^{-1} - Y_3^{1}\right) = \frac{1}{4}\sqrt{\frac{21}{2\pi}} \cdot \frac{x(4z^2 - x^2 - y^2)}{r^3}$$

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

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

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

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



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

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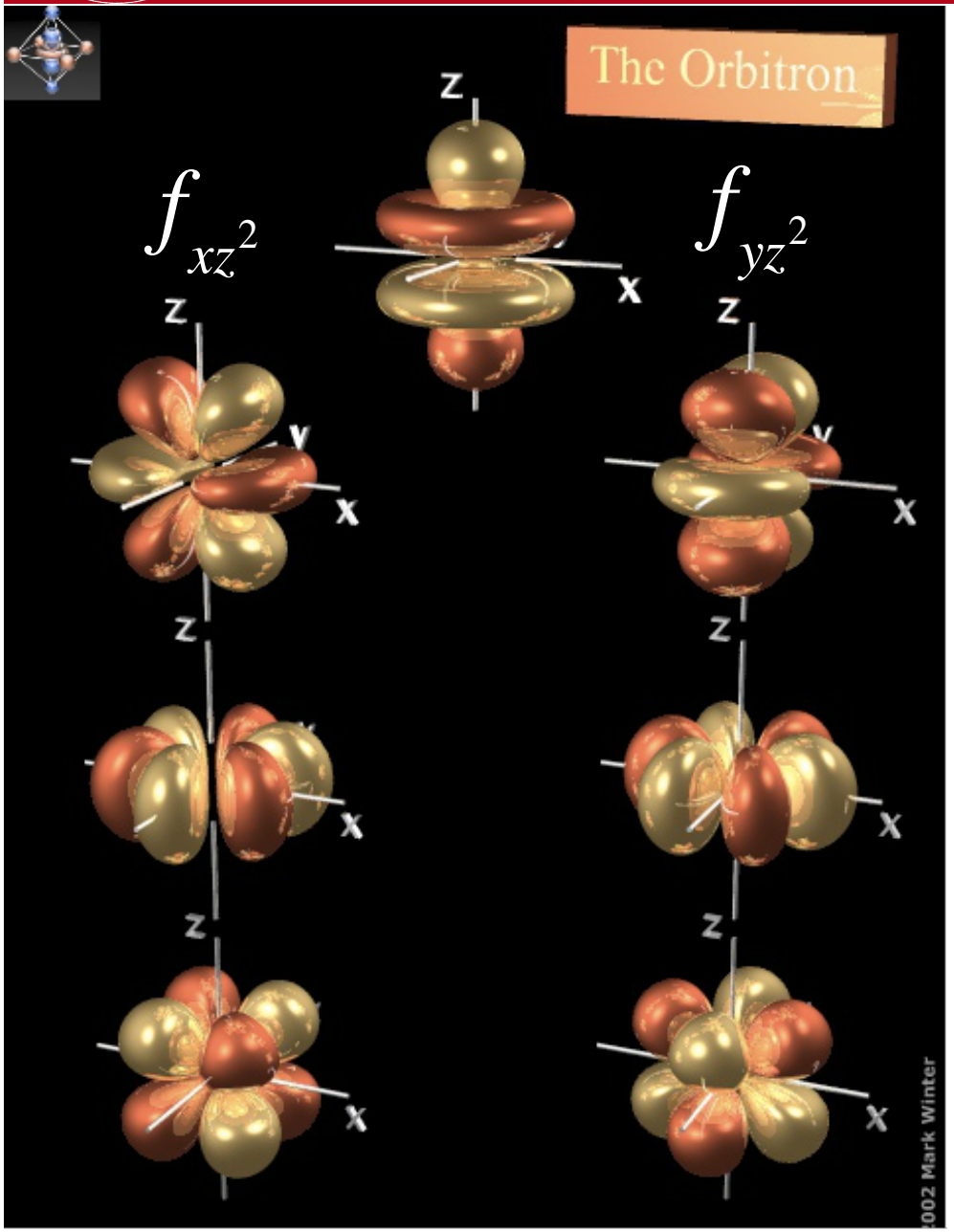

$$Y_{31} = f_{xz^2} = \sqrt{\frac{1}{2}}\left(Y_3^{-1} - Y_3^1\right) = \frac{1}{4}\sqrt{\frac{21}{2\pi}} \cdot \frac{x(4z^2 - x^2 - y^2)}{r^3}$$

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

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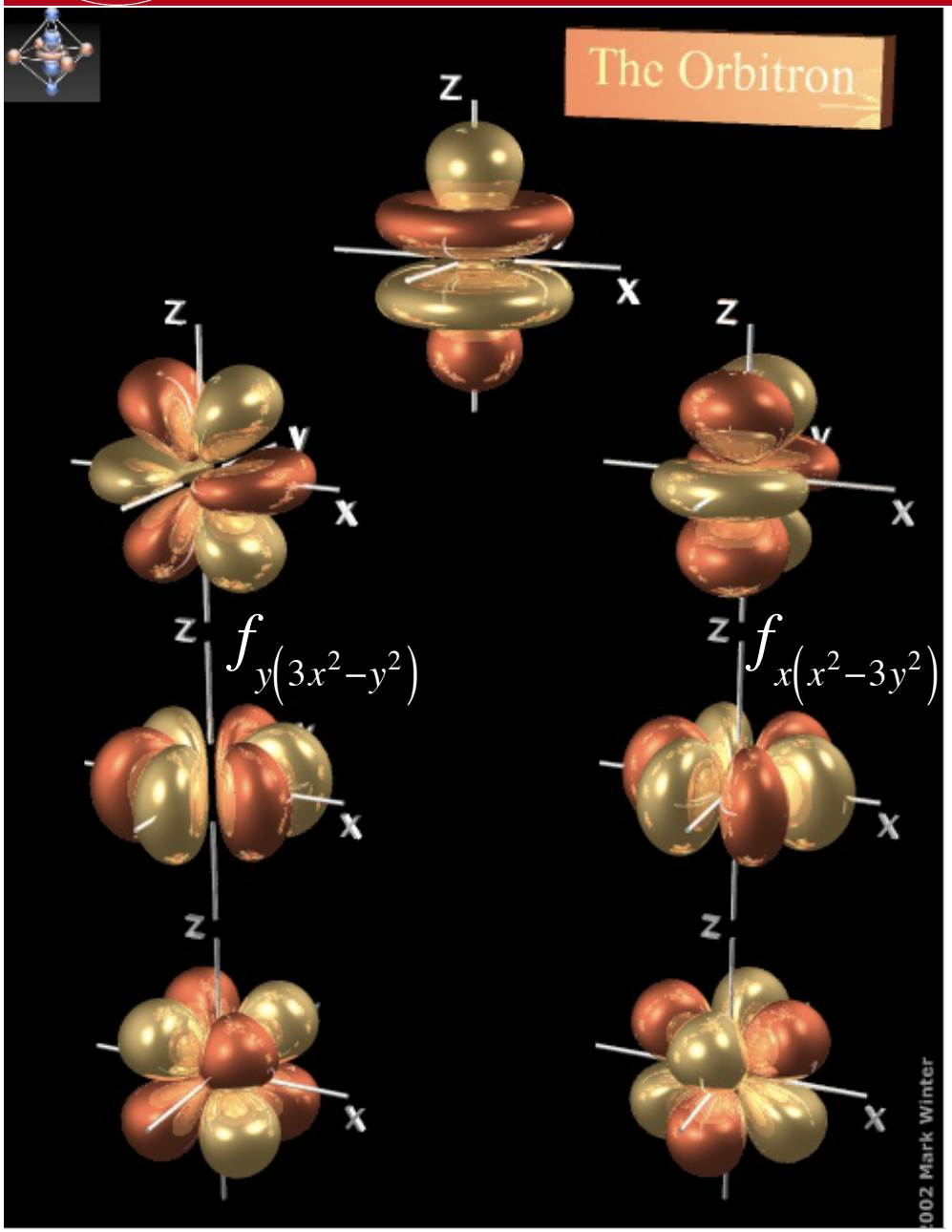
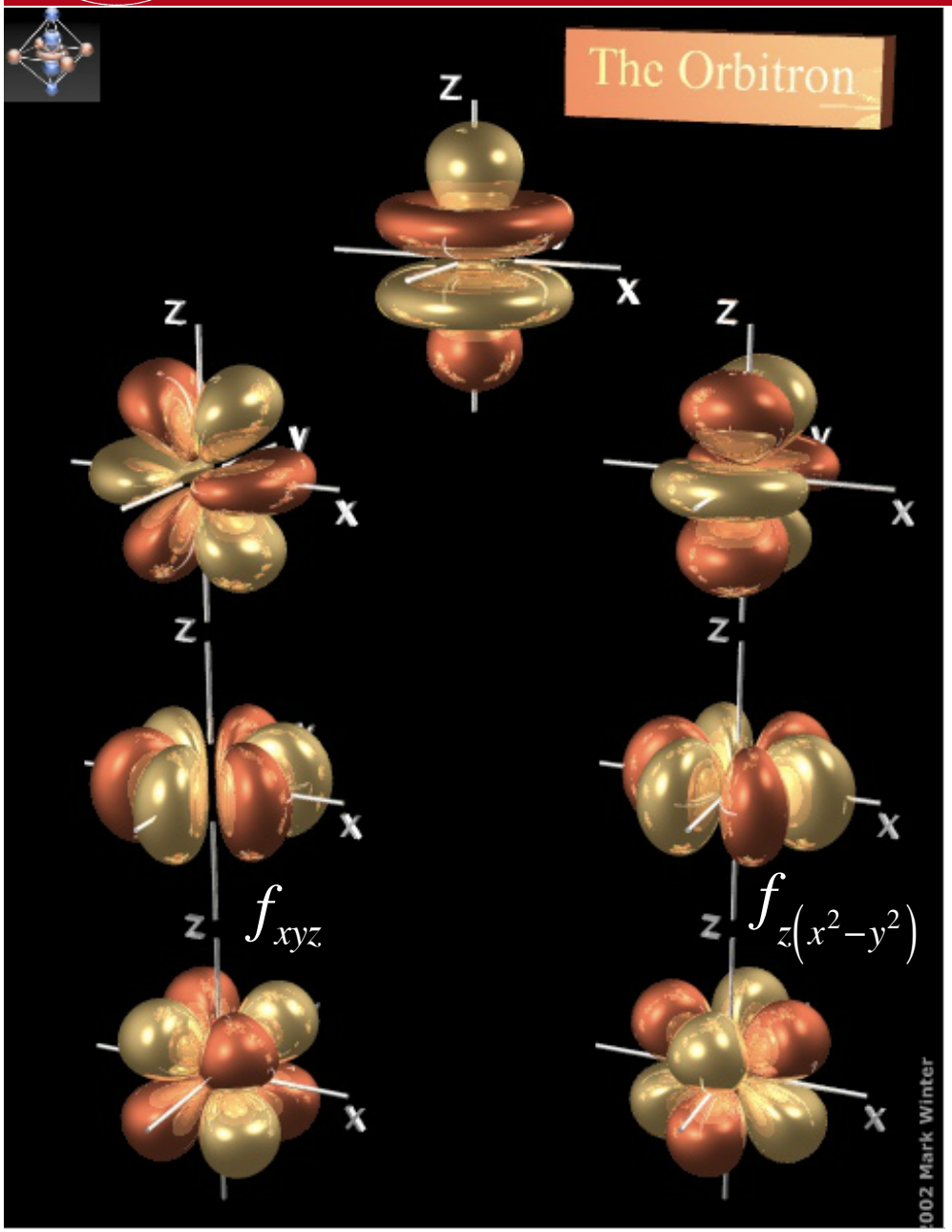


$$Y_{3,-3} = f_{y(3x^2-y^2)} = i\sqrt{\frac{1}{2}}\left(Y_3^{-3} + Y_3^3\right) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{\left(3x^2 - y^2\right) y}{r^3}$$

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

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

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



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

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

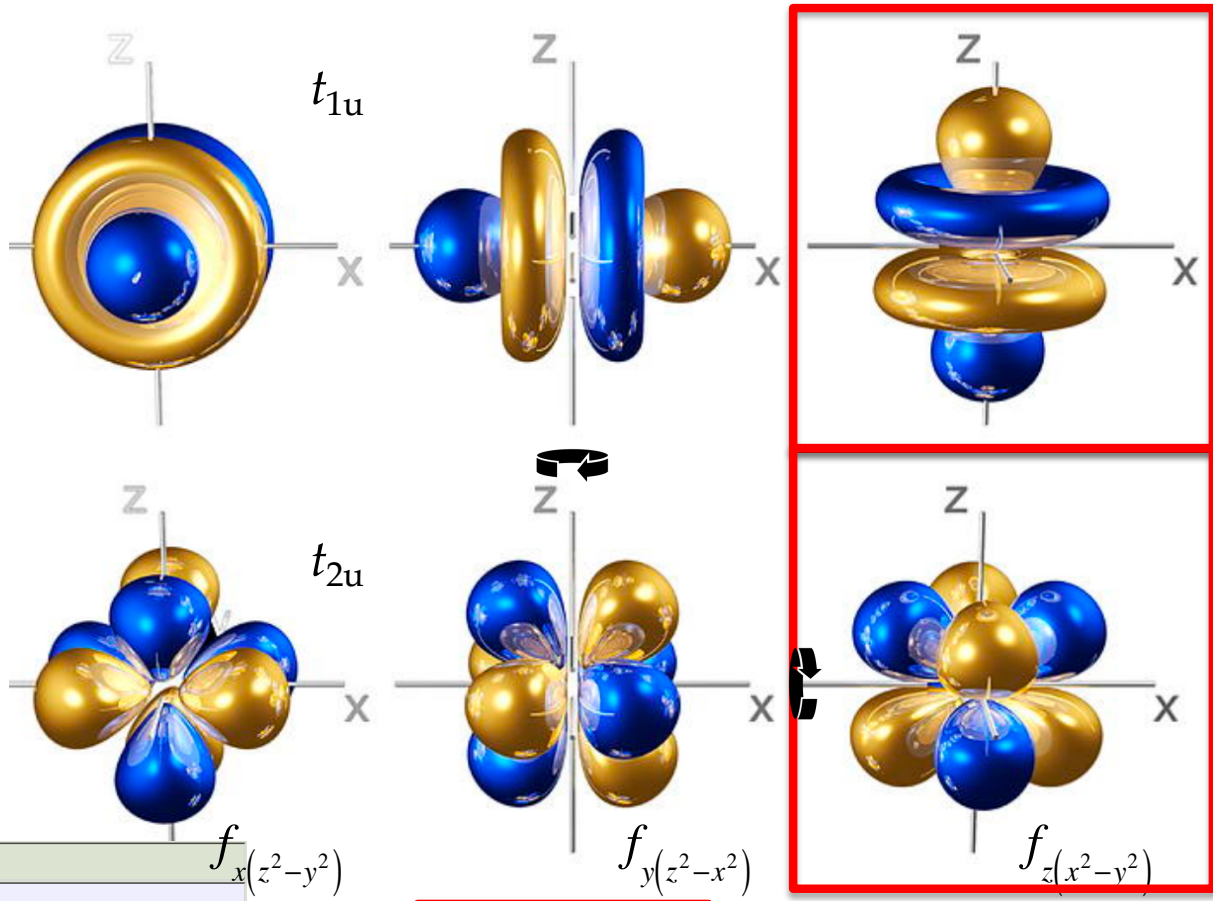
$$\rho_n \equiv \frac{2Z}{a_0 n} r$$

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

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

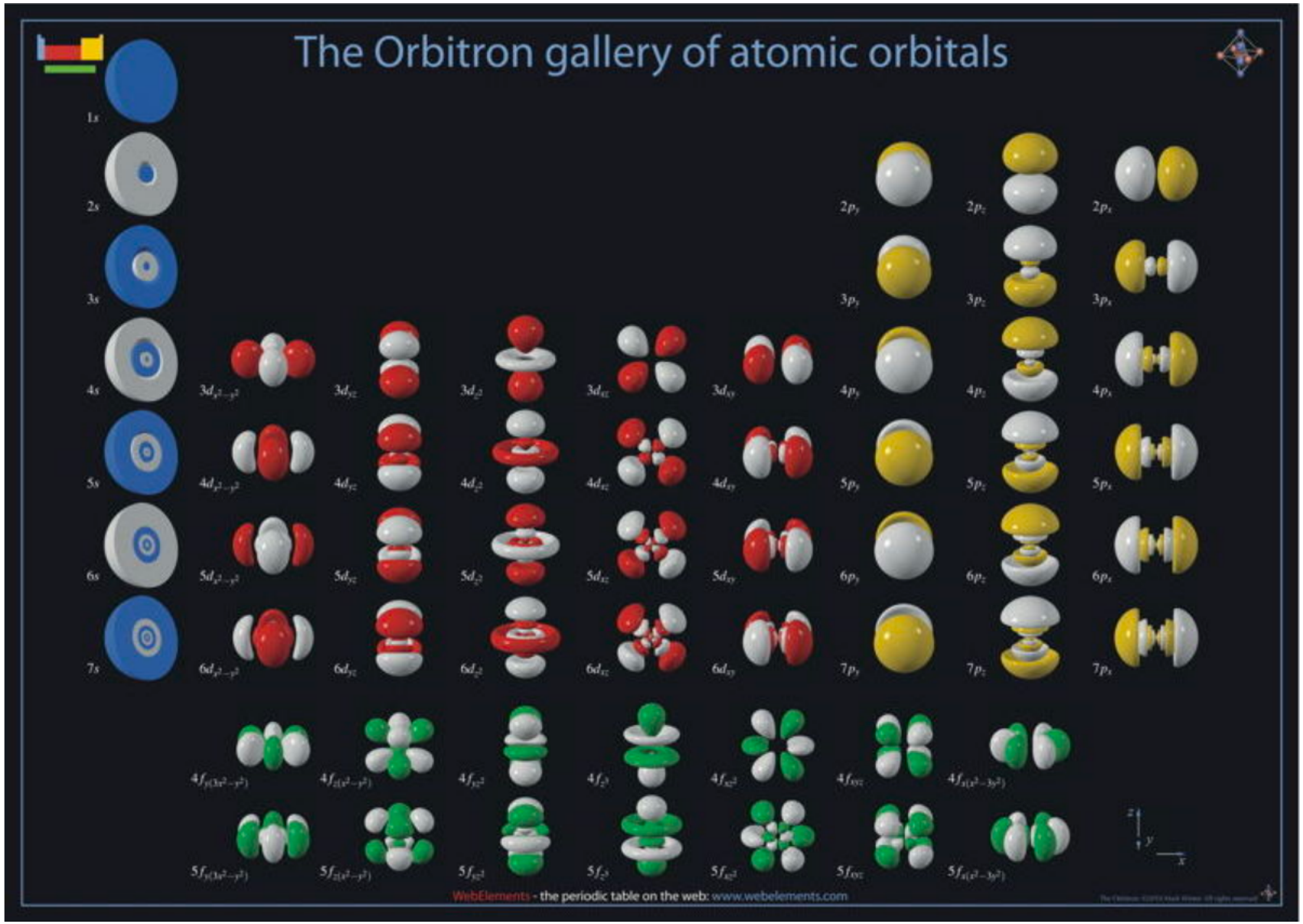
$$t_{2u}: \begin{cases} f_{z(x^2-y^2)} = f_{z(x^2-y^2)} \\ f_{x(z^2-y^2)} = \frac{1}{4}\left[\sqrt{10}Y_{31} + \sqrt{6}Y_{33}\right] \\ f_{y(z^2-x^2)} = \frac{1}{4}\left[\sqrt{10}Y_{3-1} - \sqrt{6}Y_{3-3}\right] \end{cases}$$

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



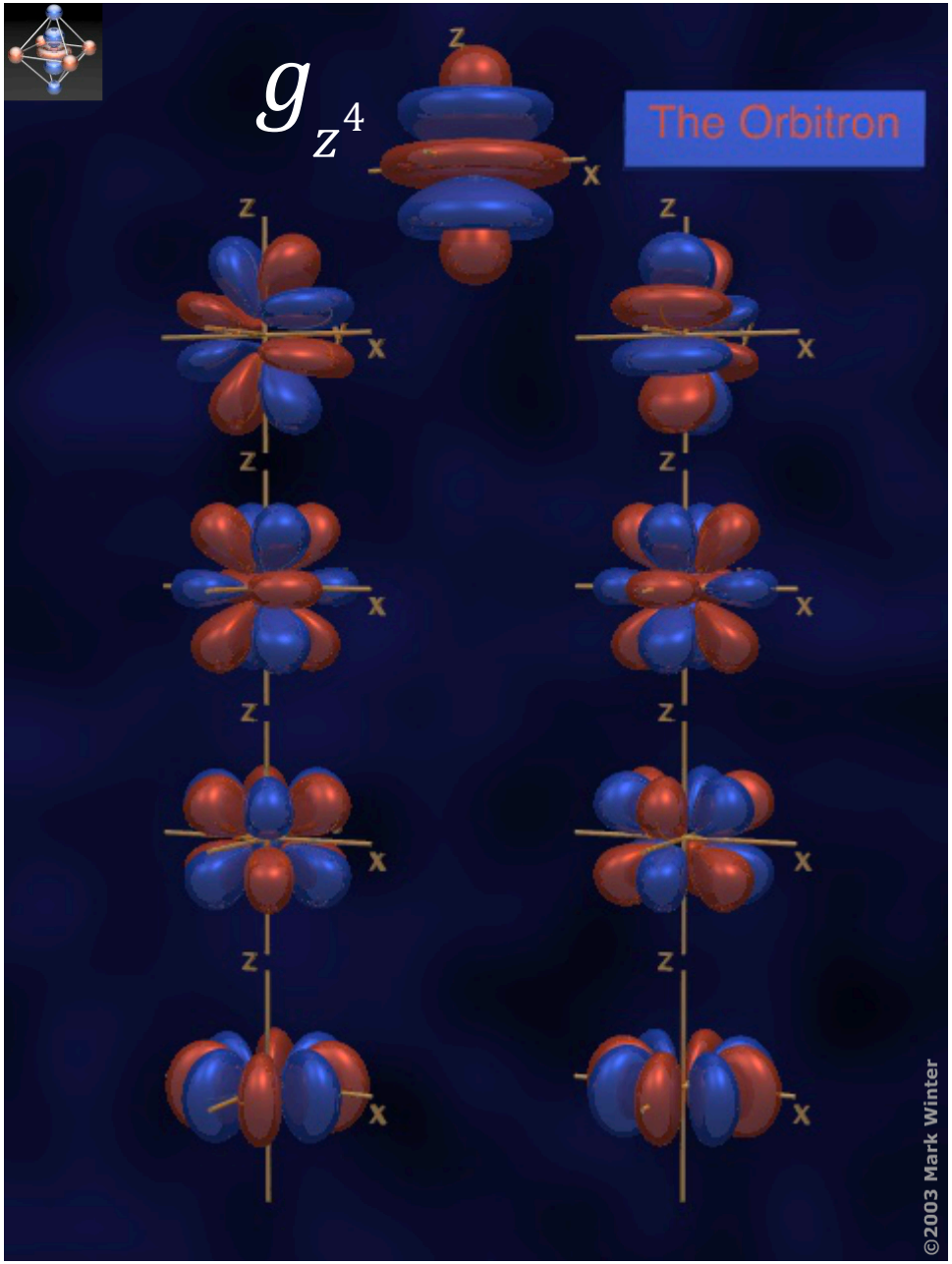
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2'$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Cubic
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1	
E_g	2	−1	0	0	2	2	0	−1	2	0	
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1	xyz
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/



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

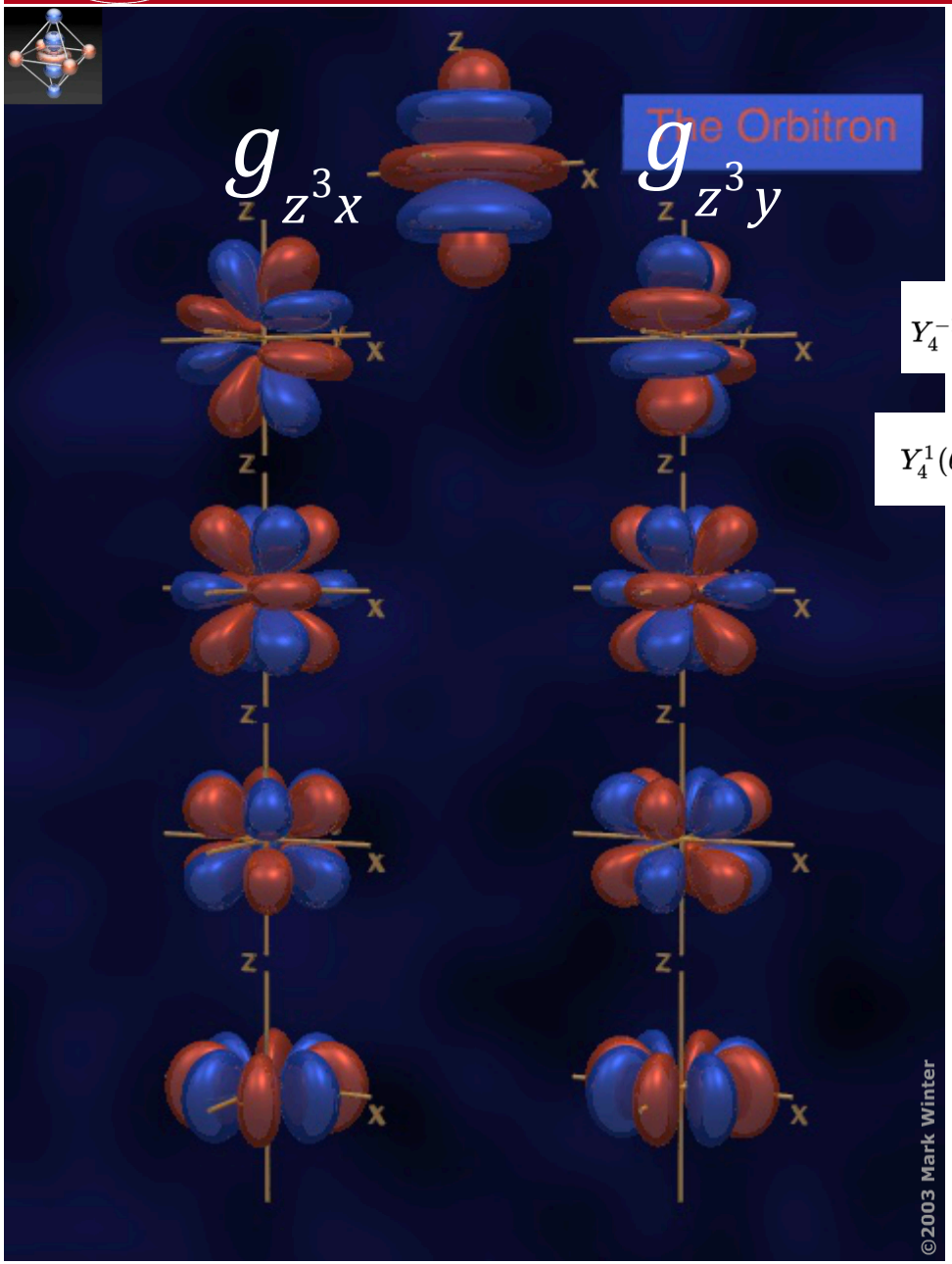
$$R_{54} = \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} \frac{1}{900\sqrt{70}} \rho_n^4$$



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

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

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

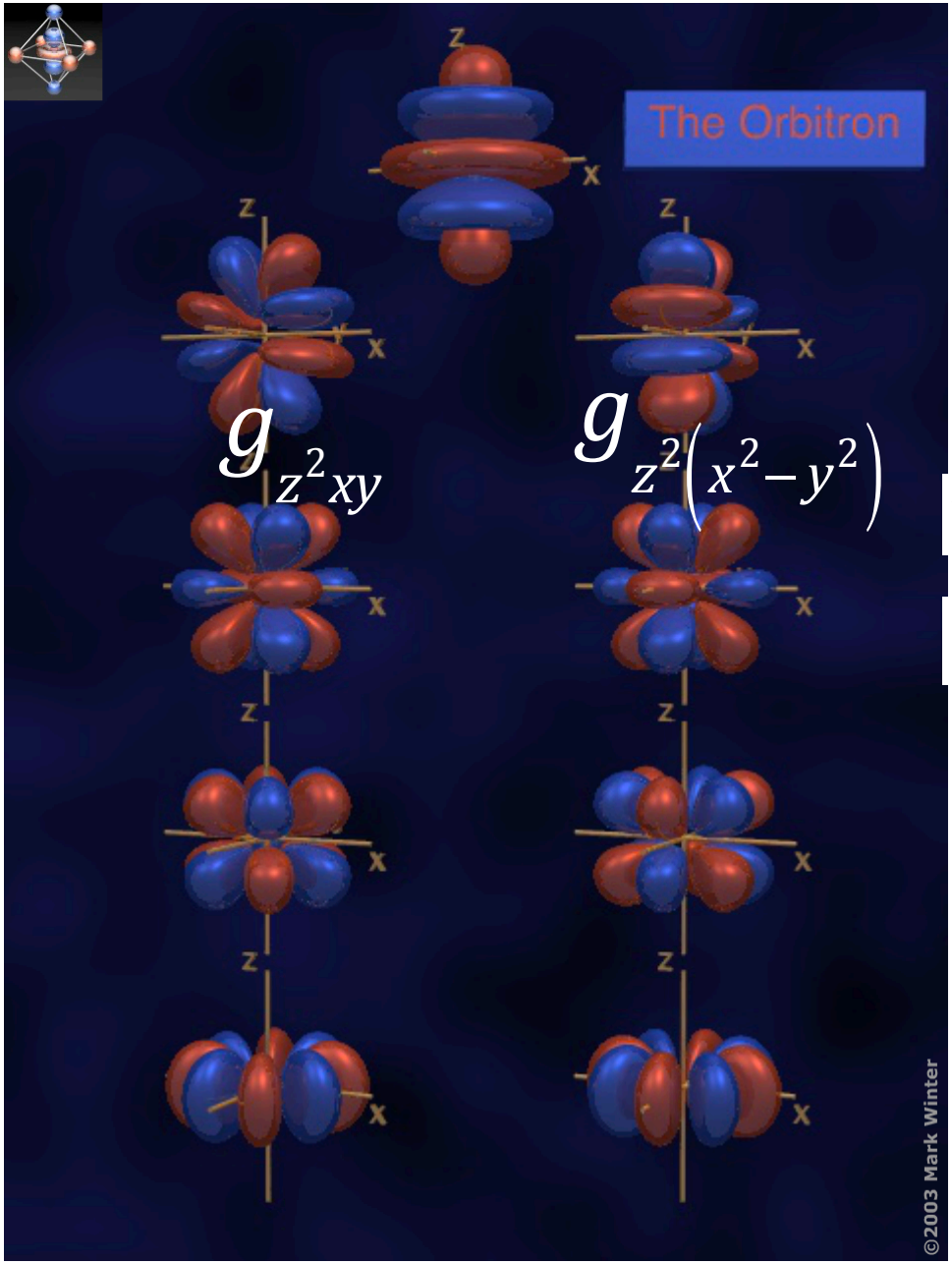


$$Y_4^{-1}(\theta,\varphi) = \frac{3}{8}\sqrt{\frac{5}{\pi}} \cdot e^{-i\varphi} \cdot \sin\theta \cdot (7\cos^3\theta - 3\cos\theta) = \frac{3}{8}\sqrt{\frac{5}{\pi}} \cdot \frac{(x-iy)\cdot z \cdot (7z^2 - 3r^2)}{r^4}$$

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

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

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



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

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

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

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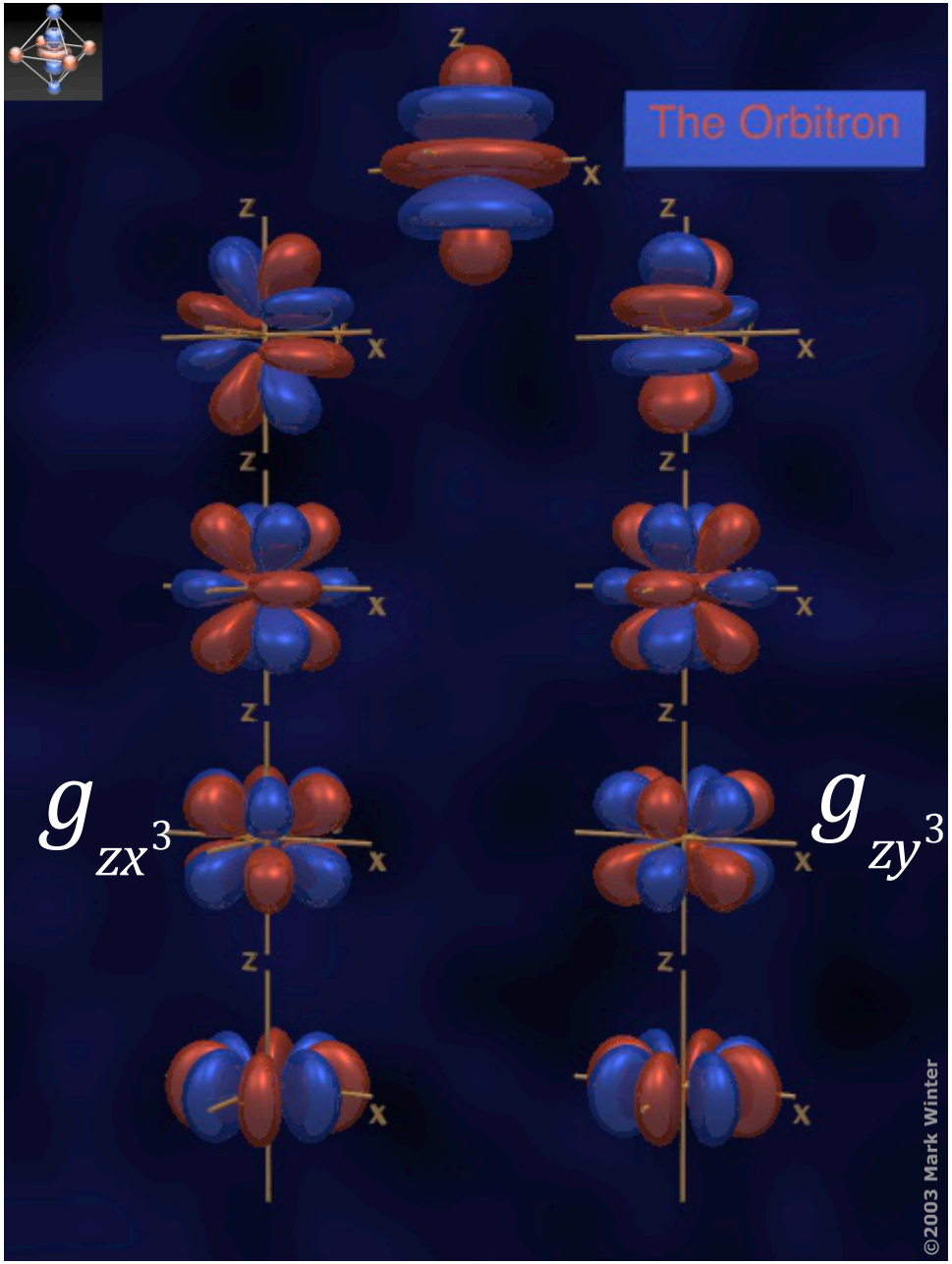
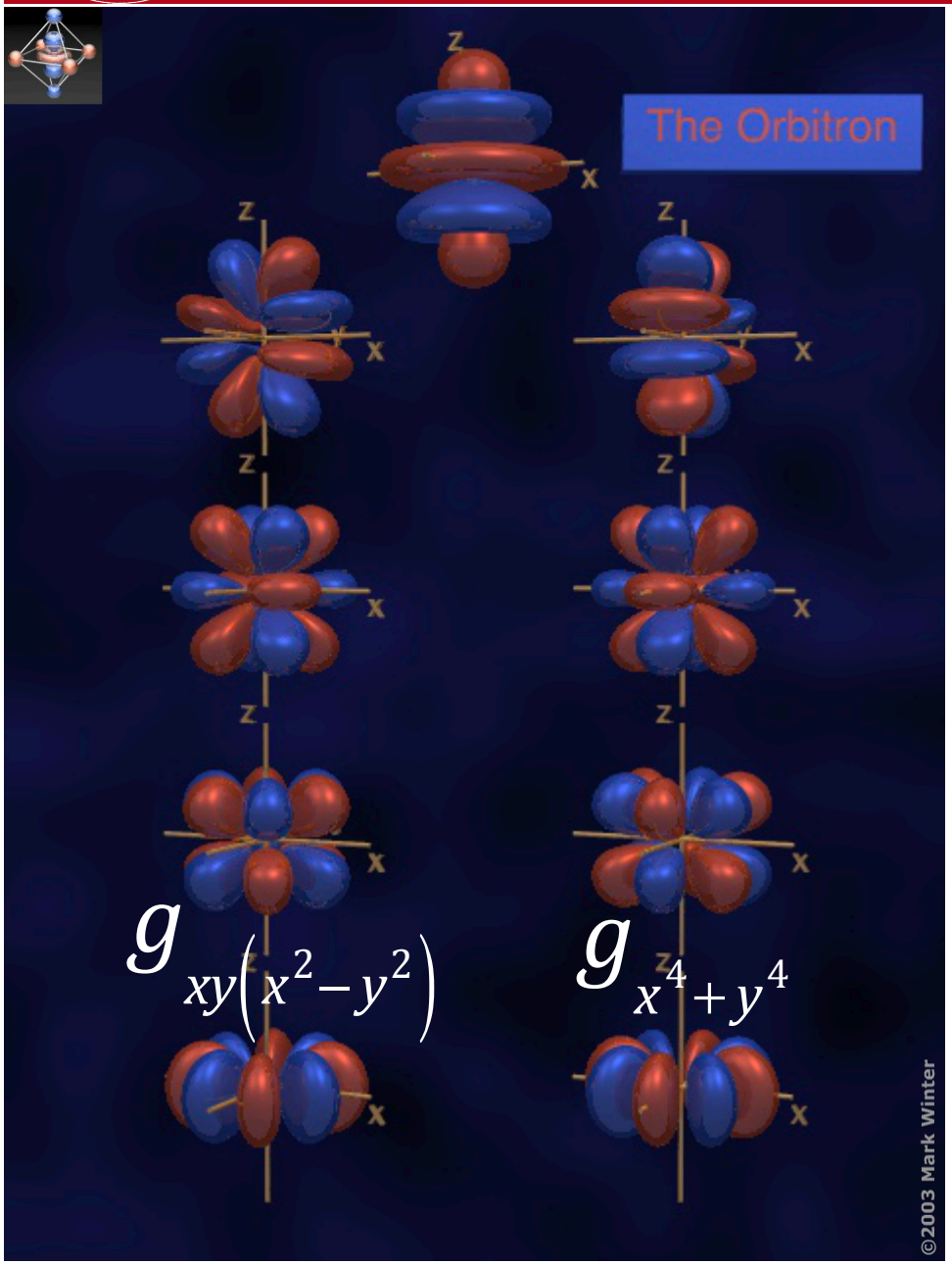


$$Y_4^{-3}(\theta,\varphi) = \frac{3}{8}\sqrt{\frac{35}{\pi}} \cdot e^{-3i\varphi} \cdot \sin^3\theta \cdot \cos\theta = \frac{3}{8}\sqrt{\frac{35}{\pi}} \cdot \frac{(x-iy)^3 z}{r^4}$$

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

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

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



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

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

ℓ = 0 (*s*)

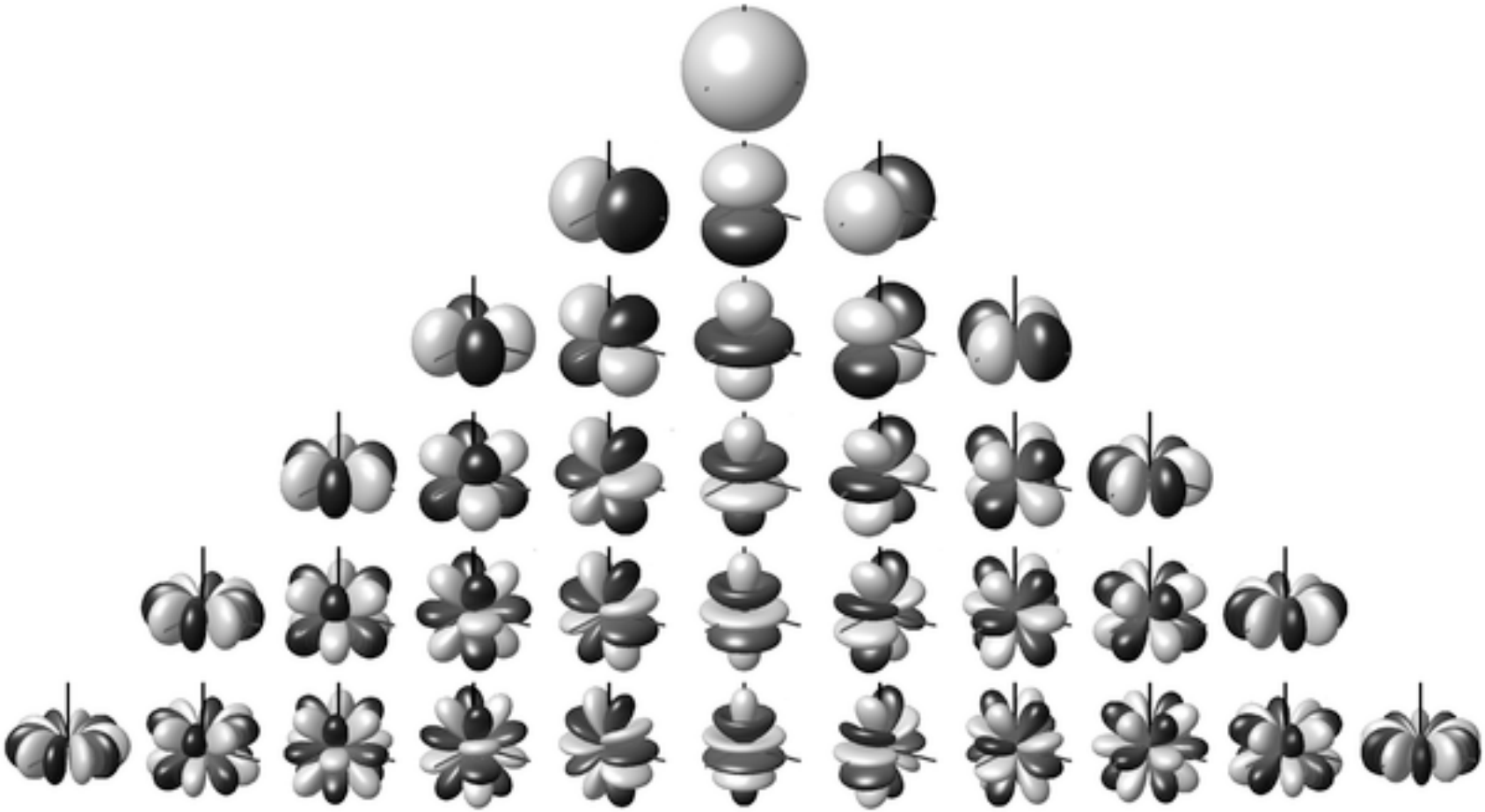
ℓ = 1 (*p*)

ℓ = 2 (*d*)

ℓ = 3 (*f*)

ℓ = 4 (*g*)

ℓ = 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	$5d^16s^2$	$4f^0$
58	Cerium	Ce	$4f^15d^16s^2$	$4f^1$
59	Praseodymium	Pr	$4f^36s^2$	$4f^2$
60	Neodymium	Nd	$4f^46s^2$	$4f^3$
61	Promethium	Pm	$4f^56s^2$	$4f^4$
62	Samarium	Sm	$4f^66s^2$	$4f^5$
63	Europium	Eu	$4f^76s^2$	$4f^6$
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^7$
65	Terbium	Tb	$4f^96s^2$	$4f^8$
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	$4f^{14}5d^16s^2$	$4f^{14}$

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

$s_1 = ½$
$S = s_1$
$2S+1 = 2$

$m_\ell \backslash m_s$	½	-½
3	3^+	3^-
2	2^+	2^-
1	1^+	1^-
0	0^+	0^-
-3	-3^+	-3^-
-2	-2^+	-2^-
-1	-1^+	-1^-

$$R_{43}(r) = \frac{1}{96\sqrt{35}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{\rho_4}{2}} \rho_4^3 \qquad \rho_4 \equiv \frac{2Z}{a_0 4} r$$

^{2}F

r = radius
π = 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)

Value of L

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

Ion	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 → S, p^1 → P, d^1 → D, f^1 → 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 occupancy (electrons or holes)							
Orbital set	0	1	2	3	4	5	6	7
s	*S*	*S*						
p	*S*	*P*	*P*	*S*				
d	*S*	*D*	*PF*	*PF*	*D*	*S*		
f	*S*	*F*	*PFH*	*SDFGI*	*SDFGI*	*PFH*	*F*	*S*
g	*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.

Partial Terms Arising from the Occupancy of a Single Spin Set[a,b]

	Orbital occupancy (electrons or holes)							
Orbital set	0	1	2	3	4	5	6	7
s	*S*	*S*						
p	*S*	*P*	*P*	*S*				
d	*S*	*D*	*PF*	*PF*	*D*	*S*		
f	*S*	*F*	*PFH*	*SDFGI*	*SDFGI*	*PFH*	*F*	*S*
g	*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.

$d_\alpha^2 d_\beta^0$

$5 \times \frac{4}{2} \times 1 = 10$ (degeneracy) $\quad (P + F) \times S \rightarrow \begin{cases} P & L = 1 \\ F & L = 3 \end{cases} \quad M_S = +1$

$d_\alpha^0 d_\beta^2$ 10 (degeneracy) $\quad S \times (P + F) \rightarrow \begin{cases} P & L = 1 \\ F & L = 3 \end{cases} \quad M_S = -1$

$d_\alpha^1 d_\beta^1$

$5 \times 5 = 25$ (degeneracy) $\quad D \times D \rightarrow \begin{cases} G & L = 4 \quad (2 + 2) \\ F & L = 3 \\ D & L = 2 \quad M_S = 0 \\ P & L = 1 \\ S & L = 0 \quad (2 - 2) \end{cases}$

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

Array for d^2

M_L	M_S = 1	0	−1
4	1		
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
−1	2	4	2
−2	1	3	1
−3	1	2	1
−4		1	

Arrays for spectral terms contained in array for d^2

M_L	M_S = 0
4	1
3	1
2	1
1	1
0	1
−1	1
−2	1
−3	1
−4	1

$L = 4$, $S = 0$, term ^1G

M_L	M_S = 1	0	−1
3	1	1	1
2	1	1	1
1	1	1	1
0	1	1	1
−1	1	1	1
−2	1	1	1
−3	1	1	1

$L = 3$, $S = 1$, term ^3F

M_L	M_S = 0
2	1
1	1
0	1
−1	1
−2	1

$L = 2$, $S = 0$, term ^1D

M_L	M_S = 1	0	−1
1	1	1	1
0	1	1	1
−1	1	1	1

$L = 1$, $S = 1$, term ^3P

M_L	M_S = 0
0	1

$L = 0$, $S = 0$, term ^1S

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

$$\underbrace{d_\alpha^3}_{5\times\frac{4}{2}} = 10 \qquad \underbrace{d_\beta^3}_{5\times\frac{4}{2}} = 10 \qquad \underbrace{d_\alpha^2}_{5\times\frac{4}{2}} d_\beta^1 = 10\times 5 = 50 \qquad d_\alpha^1 \underbrace{d_\beta^2}_{5\times\frac{4}{2}} = 5\times 10 = 50$$

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

$M_S = \pm\frac{3}{2}$ Degeneracy = 4 × 3 + 4 × 7 = 40; $M_S = \pm ½$ taken into account

$$d_\alpha^2 d_\beta^1 \left(\text{or } d_\alpha^1 d_\beta^2\right) \rightarrow {}^2\left[\left(P+F\right)\times D\right] \quad M_S = \pm\frac{1}{2}$$

$$P\times D = F + D + P \qquad \left(2+1 \le \mathrm{L} \le 2-1\right)$$

$$F\times D = H + G + F + D + P \qquad \left(3+2 \le \mathrm{L} \le 3-2\right)$$

$$d^3 \rightarrow \underbrace{\underbrace{{}^4F}_{28} + \underbrace{{}^4P}_{12} + \underbrace{{}^2H}_{22} + \underbrace{{}^2G}_{18} + \underbrace{{}^2F}_{14} + \underbrace{2\,{}^2D}_{20} + \underbrace{{}^2P}_{6}}_{120}$$

Allowed terms for *p* and *d configutarion*

	Singlets	*Doublets*	*Triplets*	*Quartets*	*Quintets*	*Sextets*
p, p^5	–	*P*	–	–	–	–
p^2, p^4	*SD*	–	*P*	–	–	–
p^3	–	*PD*	–	*S*	–	–
d, d^9	–	*D*	–	–	–	–
d^2, d^8	*SDG*	–	*PF*	–	–	–
d^3, d^7	–	*PDDFGH*	–	*PF*	–	–
d^4, d^6	*SSDDFGGI*	–	*PPDFFGH*	–	*D*	–
d^5	–	*SPDDDFFGGHI*	–	*PDFG*	–	*S*

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	Orbital occupancy (electrons or holes)							
Orbital set	0	1	2	3	4	5	6	7
s	*S*	*S*						
p	*S*	*P*	*P*	*S*				
d	*S*	*D*	*PF*	*PF*	*D*	*S*		
f	*S*	*F*	*PFH*	*SDFGI*	*SDFGI*	*PFH*	*F*	*S*
g	*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_α^3	f_β^3	$f_\alpha^2 f_\beta^1$	$f_\alpha^1 f_\beta^2$	
Degeneracy	35	35	$21 \times 7 = 147$	$7 \times 21 = 147$	Total = 364

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

$M_S = \pm\frac{3}{2}$ 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.

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

Drop ${}^2S, {}^2D, {}^2F, {}^2G, {}^2I$,

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

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

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

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
Orbital Set					
s	*S* (1)	*S* (1)			
p	*S* (1)	*P* (3)			
d	*S* (1)	*D* (5)	*PF* (10)		
f	*S* (1)	*F* (7)	*PFH* (21)	*SDF GI* (35)	
g	*S* (1)	*G* (9)	*PFHK* (36)	*PF*[2]*G HIK M* (84)	*SD*[2]*FG*[2] *HI*[2]*KLN* (126)

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