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# *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-memoire*; it can be exploited.



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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.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18						
1 H Hydrogen 25	Atomic # Symbol Name pm		<div><div>1</div><div>H</div><div>Hydrogen</div><div>1.008</div></div>															2 He Helium					
3 Li Lithium 145	4 Be Beryllium 105	<div><div>1s<sup>1</sup></div></div>																5 B Boron 85	6 C Carbon 70	7 N Nitrogen 65	8 O Oxygen 60	9 F Fluorine 50	10 Ne Neon
11 Na Sodium 180	12 Mg Magnesium 150	<div><div>1s<sup>1</sup></div></div>																13 Al Aluminum 125	14 Si Silicon 110	15 P Phosphorus 100	16 S Sulfur 105	17 Cl Chlorine 100	18 Ar Argon 71
19 K Potassium 220	20 Ca Calcium 180	21 Sc Scandium 160	22 Ti Titanium 140	23 V Vanadium 135	24 Cr Chromium 140	25 Mn Manganese 135	26 Fe Iron 140	27 Co Cobalt 135	28 Ni Nickel 135	29 Cu Copper 135	30 Zn Zinc 135	31 Ga Gallium 130	32 Ge Germanium 125	33 As Arsenic 115	34 Se Selenium 115	35 Br Bromine 115	36 Kr Krypton						
37 Rb Rubidium 235	38 Sr Strontium 200	39 Y Yttrium 180	40 Zr Zirconium 155	41 Nb Niobium 145	42 Mo Molybdenum 145	43 Tc Technetium 135	44 Ru Ruthenium 130	45 Rh Rhodium 135	46 Pd Palladium 140	47 Ag Silver 160	48 Cd Cadmium 155	49 In Indium 155	50 Sn Tin 145	51 Sb Antimony 145	52 Te Tellurium 140	53 I Iodine 140	54 Xe Xenon						
55 Cs Cesium 295	56 Ba Barium 215	57-71	72 Hf Hafnium 155	73 Ta Tantalum 145	74 W Tungsten 135	75 Re Rhenium 135	76 Os Osmium 130	77 Ir Iridium 135	78 Pt Platinum 135	79 Au Gold 150	80 Hg Mercury 160	81 Tl Thallium 190	82 Pb Lead 160	83 Bi Bismuth 160	84 Po Polonium 160	85 At Astatine	86 Rn Radon						
87 Fr Francium	88 Ra Radium 215	89-103	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson						
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57 La Lanthanum 185	58 Ce Cerium 185	59 Pr Praseodym 185	60 Nd Neodym 185	61 Pm Prometh 185	62 Sm Samarit 185	63 Eu Europium 185	64 Gd Gadolin 180	65 Tb Terbium 175	66 Dy Dyspros 175	67 Ho Holmium 175	68 Er Erbium 175	69 Tm Thulium 151	70 Yb Ytterbium 151	71 Lu Lutetium 151									
89 Ac Actinium 195	90 Th Thorium 180	91 Pa Protacti 180	92 U Uranium 175	93 Np Neptuni 175	94 Pu Plutoni 175	95 Am Americu 175	96 Cm Curium 160	97 Bk Berkeli 160	98 Cf Californ 160	99 Es Einstein 160	100 Fm Fermium 160	101 Md Mendelev 160	102 No Nobelium 160	103 Lr Lawrencium									

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

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## *Chimica Inorganica 3*

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



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1	2 He Helium 2																
3 Li Lithium 3	4 Be Beryllium 4	5 B Boron 5	6 C Carbon 6	7 N Nitrogen 7	8 O Oxygen 8	9 F Fluorine 9	10 Ne Neon 10										
11 Na Sodium 11	12 Mg Magnesium 12	13 Al Aluminum 13	14 Si Silicon 14	15 P Phosphorus 15	16 S Sulfur 16	17 Cl Chlorine 17	18 Ar Argon 18										
19 K Potassium 19	20 Ca Calcium 20	21 Sc Scandium 21	22 Ti Titanium 22	23 V Vanadium 23	24 Cr Chromium 24	25 Mn Manganese 25	26 Fe Iron 26	27 Co Cobalt 27	28 Ni Nickel 28	29 Cu Copper 29	30 Zn Zinc 30	31 Ga Gallium 31	32 Ge Germanium 32	33 As Arsenic 33	34 Se Selenium 34	35 Br Bromine 35	36 Kr Krypton 36
37 Rb Rubidium 37	38 Sr Strontium 38	39 Y Yttrium 39	40 Zr Zirconium 40	41 Nb Niobium 41	42 Mo Molybdenum 42	43 Tc Technetium 43	44 Ru Ruthenium 44	45 Rh Rhodium 45	46 Pd Palladium 46	47 Ag Silver 47	48 Cd Cadmium 48	49 In Indium 49	50 Sn Tin 50	51 Sb Antimony 51	52 Te Tellurium 52	53 I Iodine 53	54 Xe Xenon 54
55 Cs Cesium 55	56 Ba Barium 56	57-71 Lanthanides	72 Hf Hafnium 72	73 Ta Tantalum 73	74 W Tungsten 74	75 Re Rhenium 75	76 Os Osmium 76	77 Ir Iridium 77	78 Pt Platinum 78	79 Au Gold 79	80 Hg Mercury 80	81 Tl Thallium 81	82 Pb Lead 82	83 Bi Bismuth 83	84 Po Polonium 84	85 At Astatine 85	86 Rn Radon 86
87 Fr Francium 87	88 Ra Radium 88	89-103 Actinides	104 Rf Rutherfordium 104	105 Db Dubnium 105	106 Sg Seaborgium 106	107 Bh Bohrium 107	108 Hs Hassium 108	109 Mt Meitnerium 109	110 Ds Darmstadtium 110	111 Rg Roentgenium 111	112 Cn Copernicium 112	113 Nh Nihonium 113	114 Fl Flerovium 114	115 Mc Moscovium 115	116 Lv Livermorium 116	117 Ts Tennessine 117	118 Og Oganesson 118

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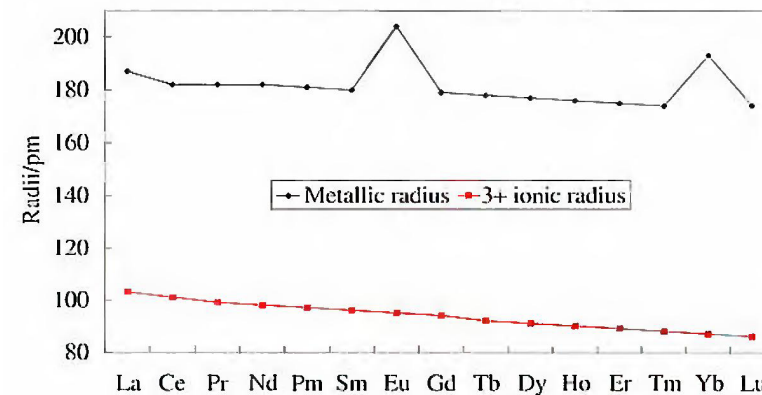
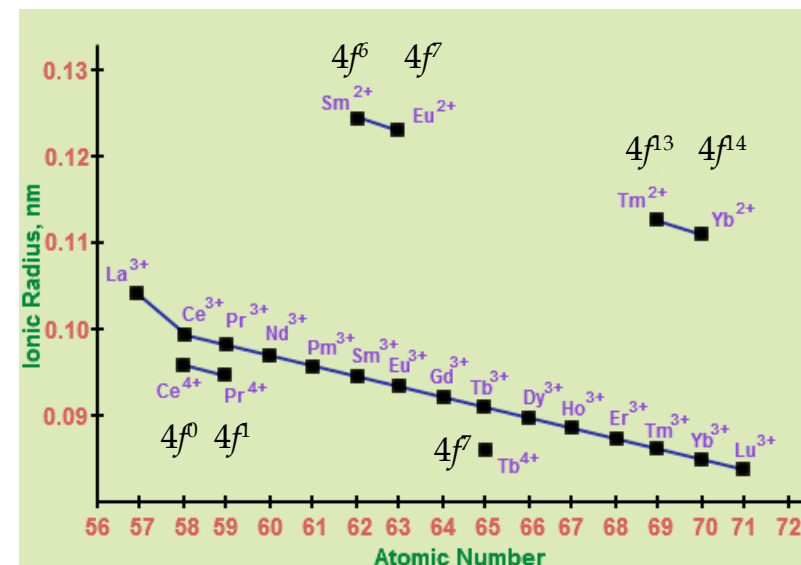


Table 1.1 The electronic configurations of lanthanide elements.

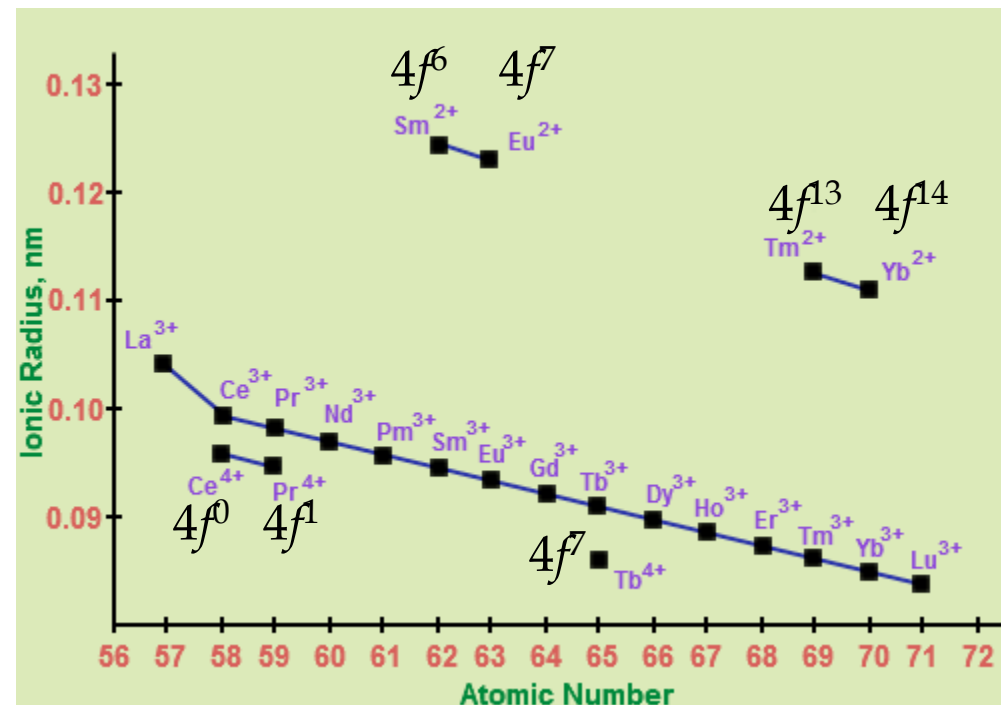
Z	Element		Electronic configurations of neutral atoms					Electronic configurations of trivalent ions		Atomic radius (pm) (coordination number = 12)	Atomic weight
			4f	5s	5p	5d	6s				
57	La	The inner	0	2	6	1	2	[Xe]4f <sup>0</sup>		187.91	138.91
58	Ce	orbitals	1	2	6	1	2	[Xe]4f <sup>1</sup>		182.47	140.12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



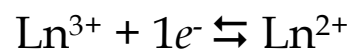


**Table 1.1** The electronic configurations of lanthanide elements.

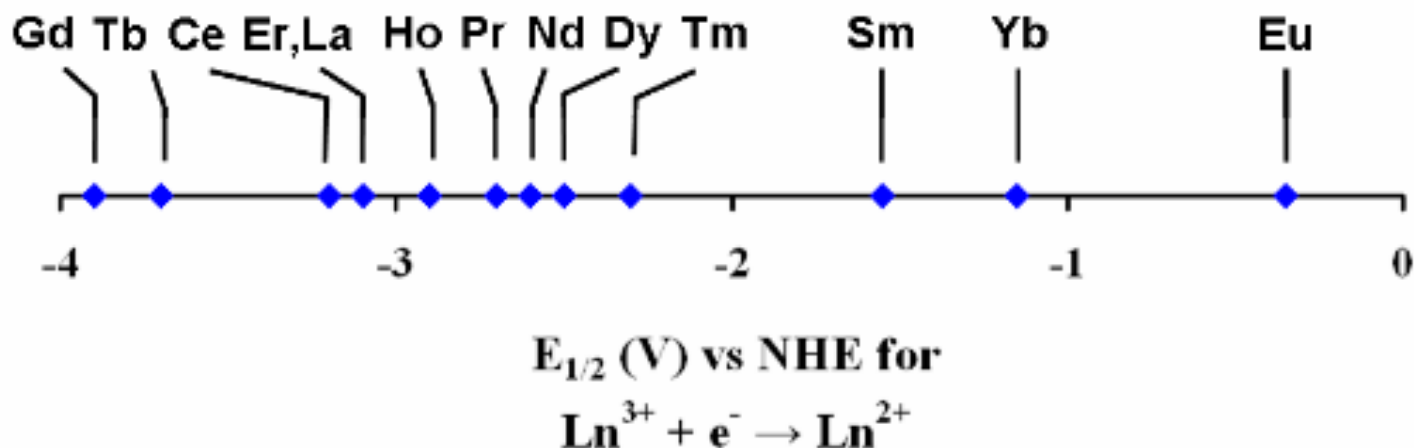
Z	Element		Electronic configurations of neutral atoms					Electronic configurations of trivalent ions	Atomic radius (pm) (coordination number = 12)	Atomic weight
			4f	5s	5p	5d	6s			
57	La	The inner	0	2	6	1	2	[Xe]4f <sup>0</sup>	187.91	138.91
58	Ce	orbitals	1	2	6	1	2	[Xe]4f <sup>1</sup>	182.47	140.12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



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



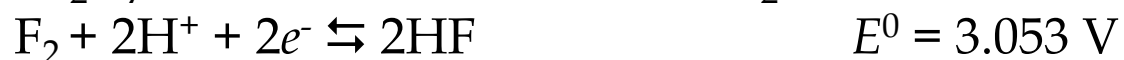
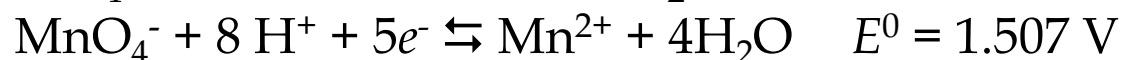
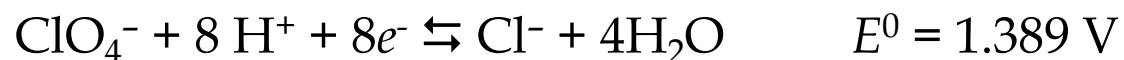
**Figure 1.** Reduction potentials for the  $\text{Ln}^{3+} + e^- \rightarrow \text{Ln}^{2+}$  process.

**Table 2.7** Redox potentials of the lanthanide ions (v)<sup>a</sup>

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$\text{Ln}^{3+} + 3e^- \rightarrow \text{Ln}$	-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
$\text{Ln}^{3+} + e^- \rightarrow \text{Ln}^{2+}$	(-3.1)	(-3.2)	(-2.7)	-2.6 <sup>b</sup>	(-2.6)	-1.55	-0.34	-3.9	(-3.7)	-2.5 <sup>b</sup>	(-2.9)	(-3.1)	-2.3 <sup>b</sup>	-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)	

<sup>a</sup> Values in parentheses are estimated.

<sup>b</sup> = in THF.



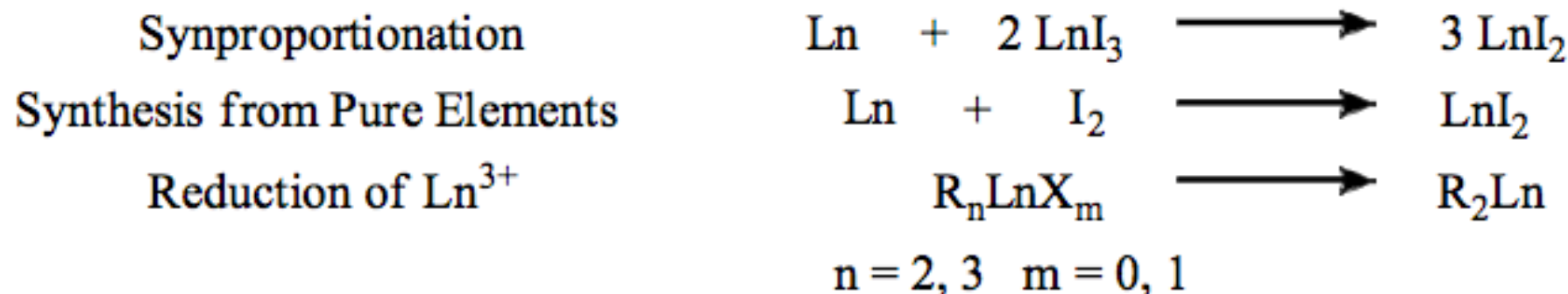


**Table 2.7** Redox potentials of the lanthanide ions (v)<sup>a</sup>

	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 <sup>b</sup>	(-2.6)	-1.55	-0.34	(-3.9)	(-3.7)	-2.5 <sup>b</sup>	(-2.9)	(-3.1)	-2.3 <sup>b</sup>	-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)	

<sup>a</sup> Values in parentheses are estimated.

<sup>b</sup> = in THF.



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



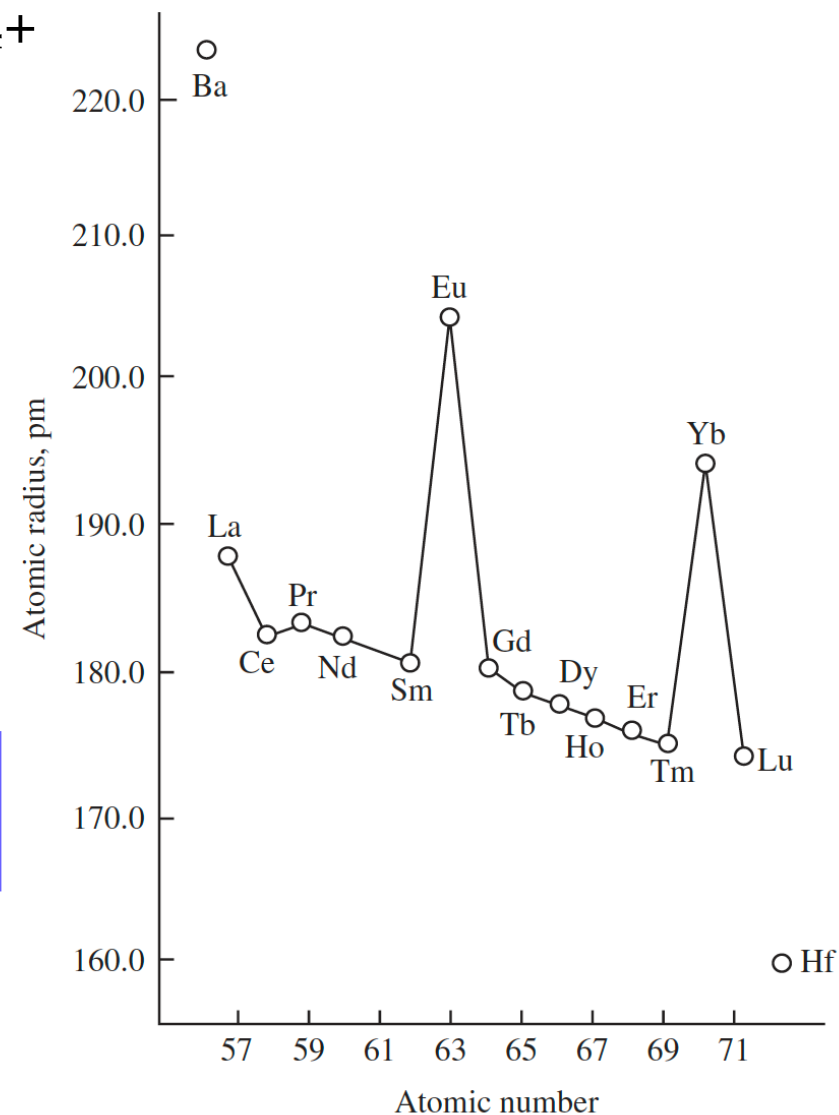
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- Size decreases across row (“lanthanide contraction”)
- Most common ion is 3+, may also be 2+ or 4+

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1 H Hydrogen 1.008	2 He Helium																
3 Li Lithium	4 Be Beryllium	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon	11 Na Sodium	12 Mg Magnesium	13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon	19 K Potassium	20 Ca Calcium
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton	37 Rb Rubidium	38 Sr Strontium
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	55 Cs Cesium	56 Ba Barium
57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten
75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon	87 Fr Francium	88 Ra Radium	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium
93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium							

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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



No radial nodes

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

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

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

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

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

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

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

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

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

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

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

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

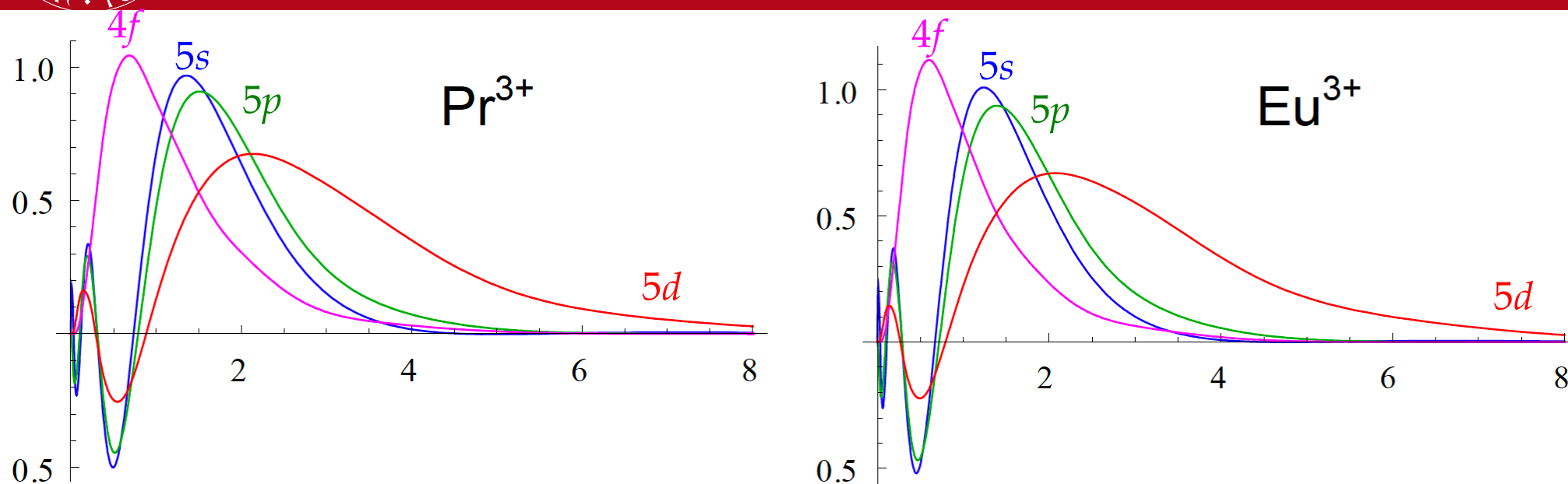
$$R_{52}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{150\sqrt{70}} (42 - 14\rho_n + \rho_n^2) \rho_n^2$$

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

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

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





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  $4f$ ,  $5s$ ,  $5p$  and  $5d$ .

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

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

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

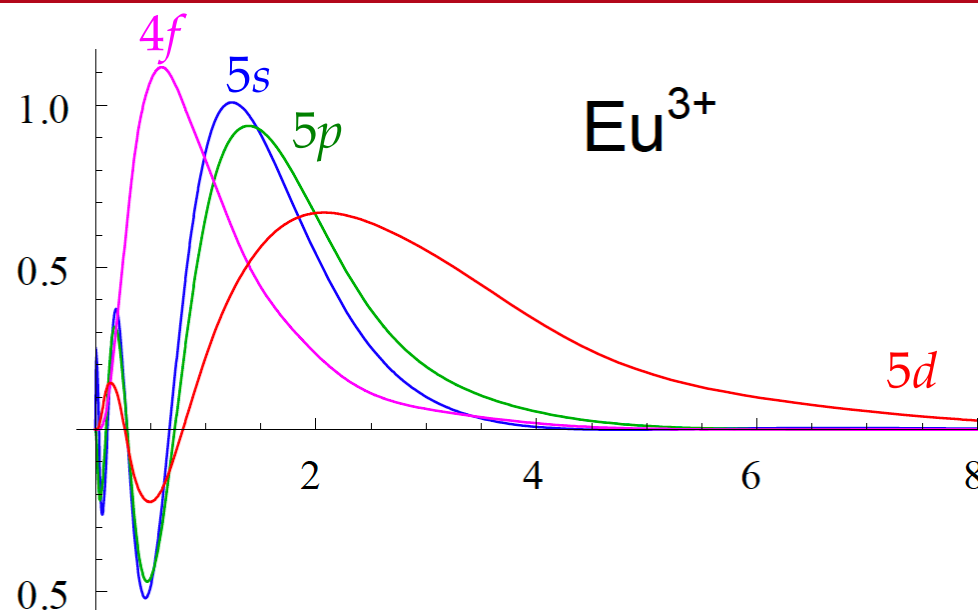
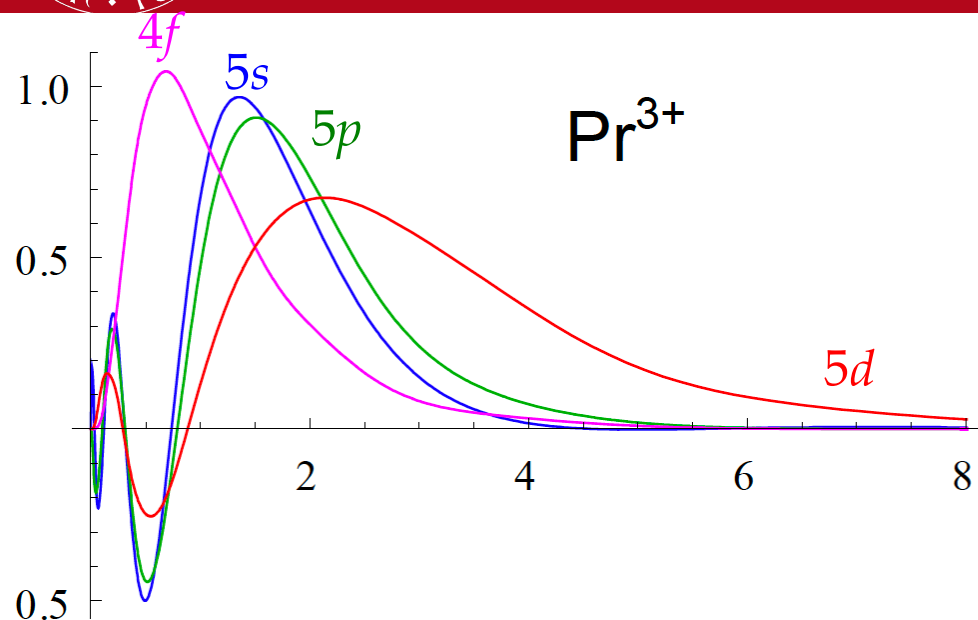
$$R_{43}(r) = \frac{1}{96\sqrt{35}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_4}{2}} \rho_4^3$$

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

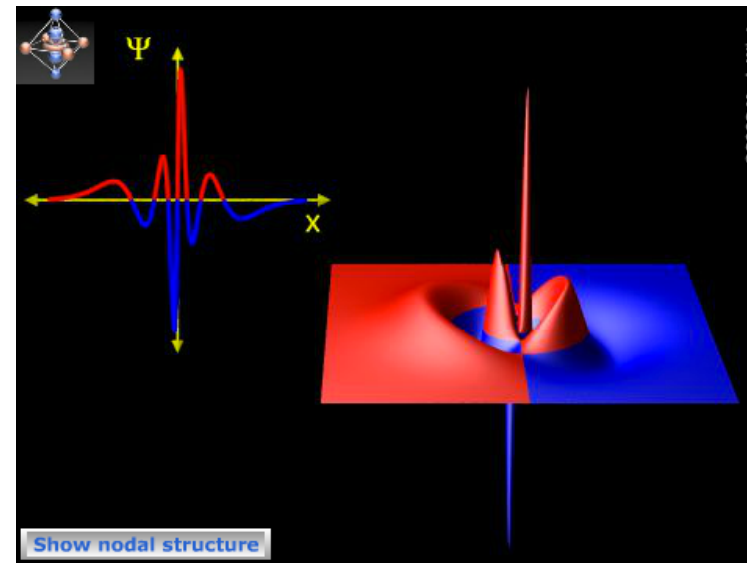
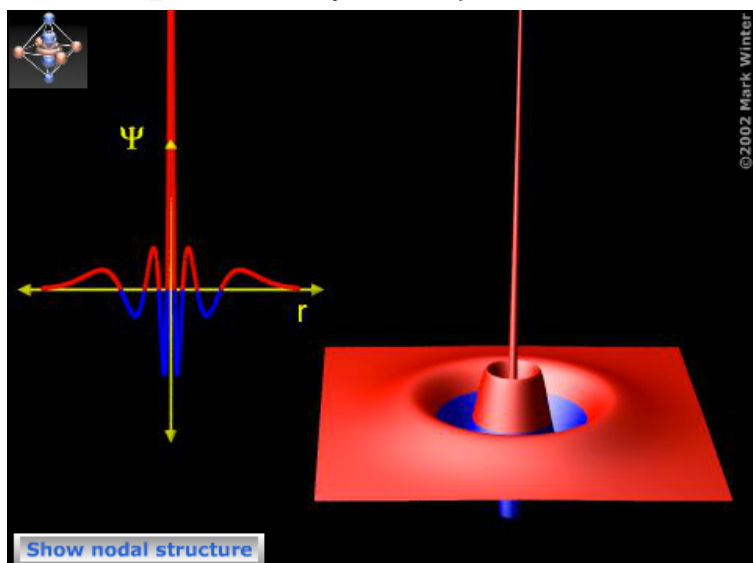


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Plots of the radial functions  $rR(r)$  vs  $r$  (in a.u.) for  $\text{Pr}(\text{III})$  and  $\text{Eu}(\text{III})$ . Pink, blue, green and red lines correspond to  $4f$ ,  $5s$ ,  $5p$  and  $5d$ .

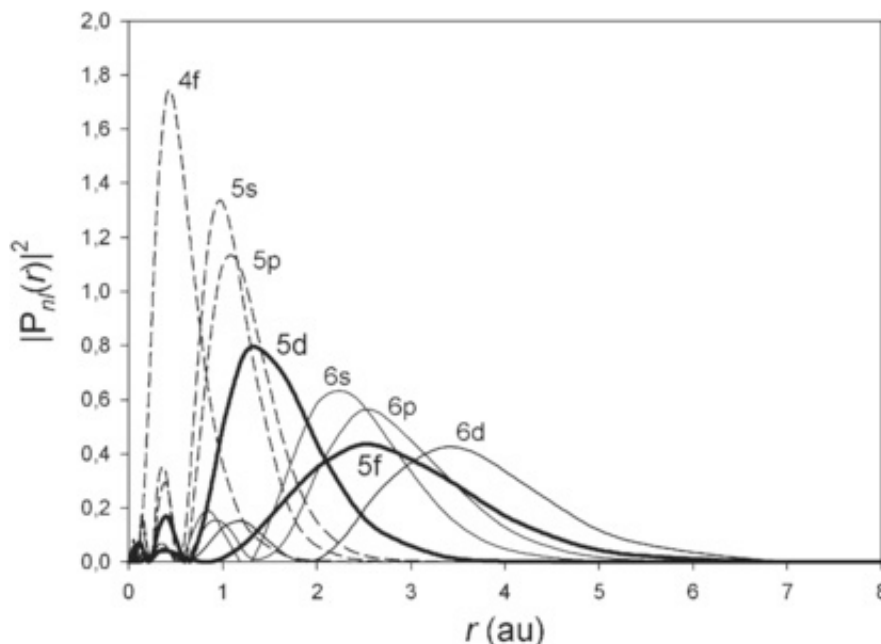




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Size decreases across row (“lanthanide contraction”)



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 Atomic Properties of the Elements																	
Frequently used fundamental physical constants																	
For the most accurate values of these and other constants, visit <a href="http://physics.nist.gov/constants">physics.nist.gov/constants</a>																	
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of <sup>133</sup> Cs																	
speed of light in vacuum $c$ 299 792 458 m s <sup>-1</sup> (exact)																	
Planck constant $h$ 6.626 07 × 10 <sup>-34</sup> J s																	
elementary charge $e$ 1.602 177 × 10 <sup>-19</sup> C																	
electron mass $m_e$ 9.109 38 × 10 <sup>-31</sup> kg																	
proton mass $m_p$ 1.672 622 × 10 <sup>-27</sup> kg																	
fine-structure constant $\alpha$ 1/137.035 999																	
Rydberg constant $R_\infty$ 10 973 731.568 m <sup>-1</sup>																	
atomic $R_\infty$ 3.289 841 960 × 10 <sup>10</sup> Hz																	
$R_\infty hc$ 13.605 69 eV																	
$k$ 1.380 6 × 10 <sup>-23</sup> J K <sup>-1</sup>																	
Boltzmann constant																	
Legend: Solids (blue), Liquids (green), Gases (red), Artificially Prepared (yellow)																	
NIST National Institute of Standards and Technology U.S. Department of Commerce																	
Physical Measurement Laboratory www.nist.gov/pml																	
Standard Reference Data www.nist.gov/srd																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar
Hydrogen	Helium	Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon	Sodium	Magnesium	Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon
1.008	4.002602	6.941	9.0121831	10.811	12.011	14.007	15.999	18.99840316	20.1797	22.98976928	24.305	26.9815385	28.0855	30.9737620	32.06	35.45	39.948
[1s] 1s	[1s] 1s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s	[1s] 2s
13.9984	13.9984	5.3917	9.3227	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917	5.3917
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton
39.0983	40.078	44.955908	47.867	50.9415	51.9961	54.938044	55.845	58.933194	58.6934	63.546	65.38	69.723	72.630	74.921595	78.971	79.904	83.798
[Ar] 4s	[Ar] 4s	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d	[Ar] 3d
4.3711	6.1132	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615	6.5615
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon
85.4678	87.62	88.90584	91.224	92.90637	95.93	98.90625	101.07	101.07	106.42	107.8682	112.414	114.818	118.710	121.757	127.60	126.90547	131.29
[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d	[Kr] 4d
4.7171	5.6949	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173	6.2173
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Cesium	Barium	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	
132.9054520	137.327	140.116	140.116	140.907	144.242	144.242	150.36	151.964	157.25	158.92535	162.500	164.93032	167.259	168.93422	173.054	174.9668	
[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d	[Xe] 5d
4.8839	5.2117	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789	5.5789
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
Francium	Radium	Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lutetium	
(223)	(226)	(227)	232.0377	231.03688	238.02891	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)	
[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s	[Rn] 7s
4.7777	5.2784	5.3802	6.3067	5.89	6.1941	6.2655	6.2655	5.9738	5.9738	5.9738	5.9738	5.9738	5.9738	5.9738	5.9738	5.9738	5.9738
Lanthanides																	
Actinides																	
Atomic Number																	
Ground-state Level																	
Symbol																	
Name																	
Standard Atomic Weight																	
Ground-state Configuration																	
Ionization Energy (eV)																	
IUPAC conventional atomic weights; standard atomic weights for these elements are expressed in intervals; see <a href="http://iupac.org">iupac.org</a> for an explanation and values.																	
For a description of the data, visit <a href="http://physics.nist.gov/data">physics.nist.gov/data</a>																	
NIST SP 966 (September 1994)																	

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.



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- 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 <b>H</b> Idrogeno 1.008	2 <b>He</b> Elio 4.003	3 <b>Li</b> Litio 6.941	4 <b>Be</b> Berillio 9.012	5 <b>B</b> Boro 10.81	6 <b>C</b> Carbonio 12.011	7 <b>N</b> Azoto 14.007	8 <b>O</b> Ossigeno 15.999	9 <b>F</b> Fluoro 18.998	10 <b>Ne</b> Neon 20.180	11 <b>Na</b> Sodio 22.990	12 <b>Mg</b> Magnesio 24.305	13 <b>Al</b> Alluminio 26.982	14 <b>Si</b> Silicio 28.086	15 <b>P</b> Fosforo 30.974	16 <b>S</b> Zolfo 32.06	17 <b>Cl</b> Cloro 35.45	18 <b>Ar</b> Argon 39.948
19 <b>K</b> Potassio 39.098	20 <b>Ca</b> Calcio 40.078	21 <b>Sc</b> Scandio 44.956	22 <b>Ti</b> Titanio 47.88	23 <b>V</b> Vanadio 50.942	24 <b>Cr</b> Cromo 52.00	25 <b>Mn</b> Manganese 54.938	26 <b>Fe</b> Ferro 55.845	27 <b>Co</b> Cobalto 58.933	28 <b>Ni</b> Nichel 58.69	29 <b>Cu</b> Rame 63.546	30 <b>Zn</b> Zinco 65.38	31 <b>Ga</b> Gallio 69.723	32 <b>Ge</b> Germanio 72.64	33 <b>As</b> Arsenico 74.922	34 <b>Se</b> Selenio 78.96	35 <b>Br</b> Bromo 79.904	36 <b>Kr</b> Kripton 83.80
37 <b>Rb</b> Rubidio 85.468	38 <b>Sr</b> Stronzio 87.62	39 <b>Y</b> Ittrio 88.906	40 <b>Zr</b> Zirconio 91.224	41 <b>Nb</b> Niobio 92.906	42 <b>Mo</b> Molibdeno 95.94	43 <b>Tc</b> Tecnezio 98.906	44 <b>Ru</b> Rutenio 101.07	45 <b>Rh</b> Rodio 102.91	46 <b>Pd</b> Palladio 106.42	47 <b>Ag</b> Argento 107.87	48 <b>Cd</b> Cadmio 112.41	49 <b>In</b> Indio 114.82	50 <b>Sn</b> Stagno 118.71	51 <b>Sb</b> Antimonio 121.76	52 <b>Te</b> Tellurio 127.6	53 <b>I</b> Iodio 126.91	54 <b>Xe</b> Xeno 131.29
55 <b>Cs</b> Cesio 132.91	56 <b>Ba</b> Bario 137.33	57-71 <b>Lanthanides</b>	72 <b>Hf</b> Afnio 178.49	73 <b>Ta</b> Tantalio 180.95	74 <b>W</b> Tungsteno 183.84	75 <b>Re</b> Renio 186.21	76 <b>Os</b> Osmio 190.23	77 <b>Ir</b> Iridio 192.22	78 <b>Pt</b> Platino 195.08	79 <b>Au</b> Oro 196.97	80 <b>Hg</b> Mercurio 200.59	81 <b>Tl</b> Tallio 204.38	82 <b>Pb</b> Piombo 207.2	83 <b>Bi</b> Bismuto 208.98	84 <b>Po</b> Polonio 209	85 <b>At</b> Astatio 210	86 <b>Rn</b> Radon 222
87 <b>Fr</b> Francio 223	88 <b>Ra</b> Radio 226	89-103 <b>Actinides</b>	104 <b>Rf</b> Rutherfordio 261	105 <b>Db</b> Dubnio 262	106 <b>Sg</b> Seaborgio 266	107 <b>Bh</b> Bohrio 264	108 <b>Hs</b> Hassio 277	109 <b>Mt</b> Meitnerio 268	110 <b>Ds</b> Darmstadtio 271	111 <b>Rg</b> Roentgenio 272	112 <b>Cn</b> Copernicio 285	113 <b>Nh</b> Nihonium 284	114 <b>Fl</b> Flerovio 289	115 <b>Mc</b> Moscovio 288	116 <b>Lv</b> Livermorio 293	117 <b>Ts</b> Tennessio 289	118 <b>Og</b> Oganesson 294

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

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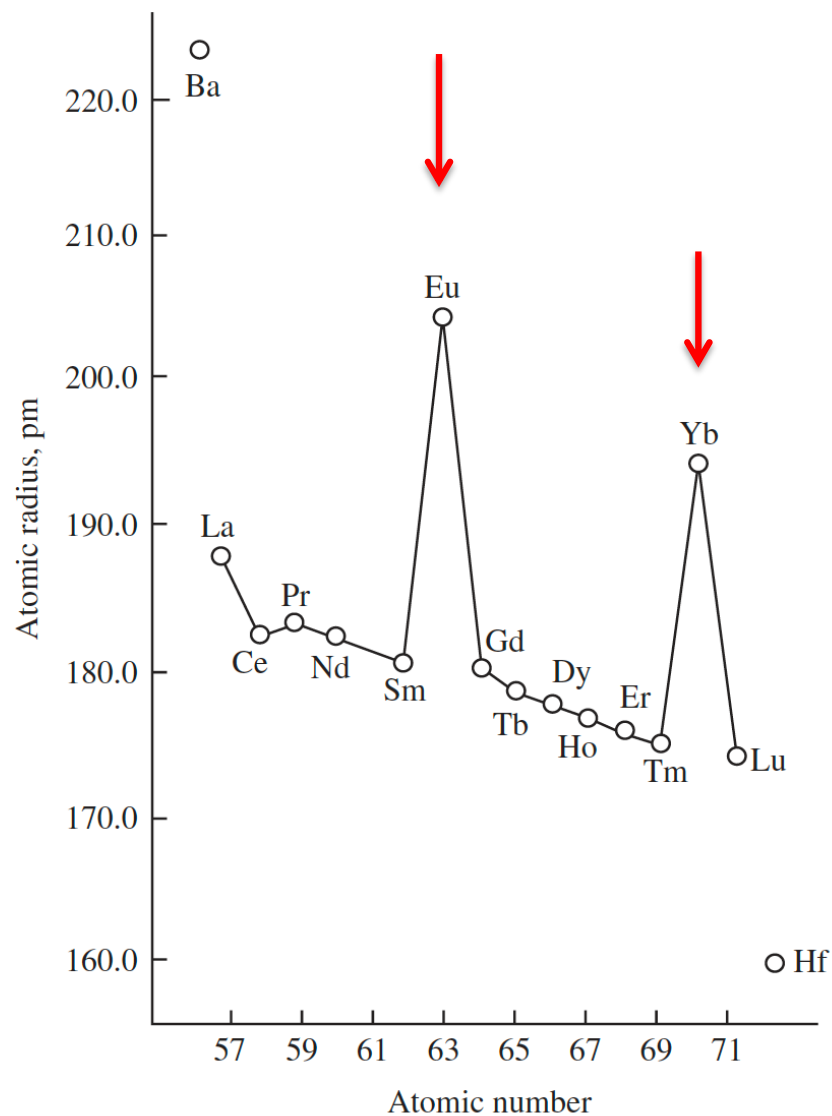
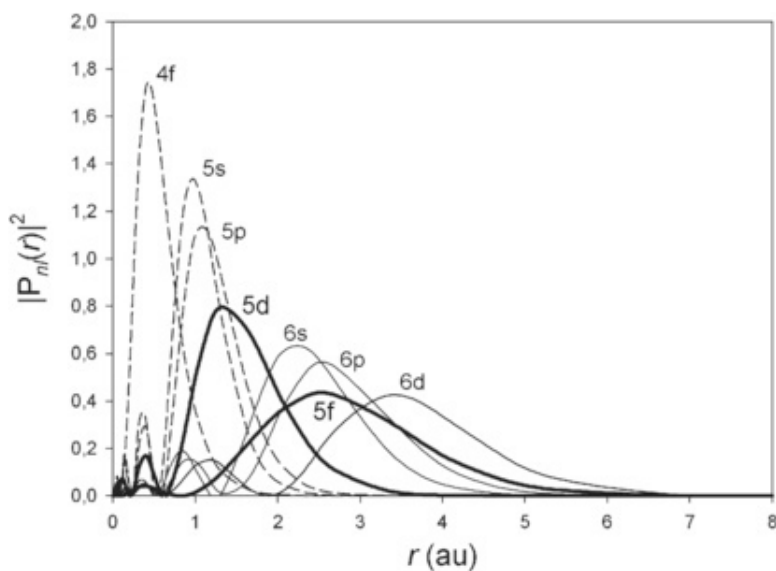
57 <b>La</b> Lantanio 138.905	58 <b>Ce</b> Cerio 140.12	59 <b>Pr</b> Praseodimio 140.908	60 <b>Nd</b> Neodimio 144.24	61 <b>Pm</b> Promezio 145	62 <b>Sm</b> Samario 150.36	63 <b>Eu</b> Europio 151.964	64 <b>Gd</b> Gadolinio 157.25	65 <b>Tb</b> Terbio 158.925	66 <b>Dy</b> Disprosio 162.50	67 <b>Ho</b> Olmio 164.930	68 <b>Er</b> Erbio 167.259	69 <b>Tm</b> Tulio 168.933	70 <b>Yb</b> Itterbio 173.054	71 <b>Lu</b> Lutezio 174.967
89 <b>Ac</b> Attinio 227.033	90 <b>Th</b> Torio 232.038	91 <b>Pa</b> Protattinio 231.036	92 <b>U</b> Uranio 238.029	93 <b>Np</b> Nettunio 237.048	94 <b>Pu</b> Plutonio 244.064	95 <b>Am</b> Americio 243.061	96 <b>Cm</b> Curio 247.070	97 <b>Bk</b> Berkelio 247.070	98 <b>Cf</b> Californio 251.083	99 <b>Es</b> Einsteinio 252.083	100 <b>Fm</b> Fermio 257.105	101 <b>Md</b> Mendelevio 258.10	102 <b>No</b> Nobelio 259.108	103 <b>Lr</b> Laurenzio 262.105



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





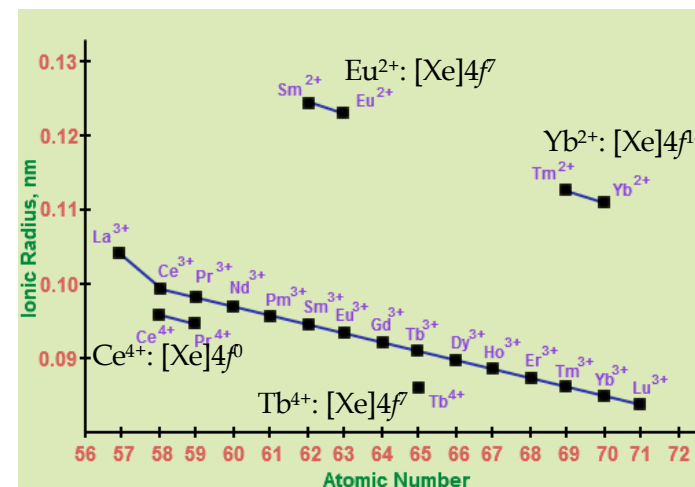
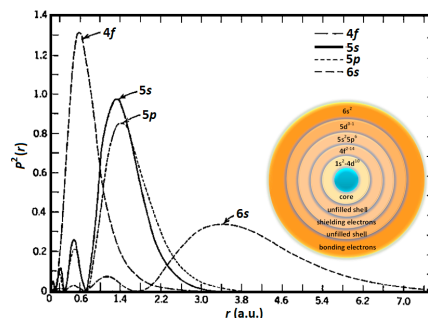
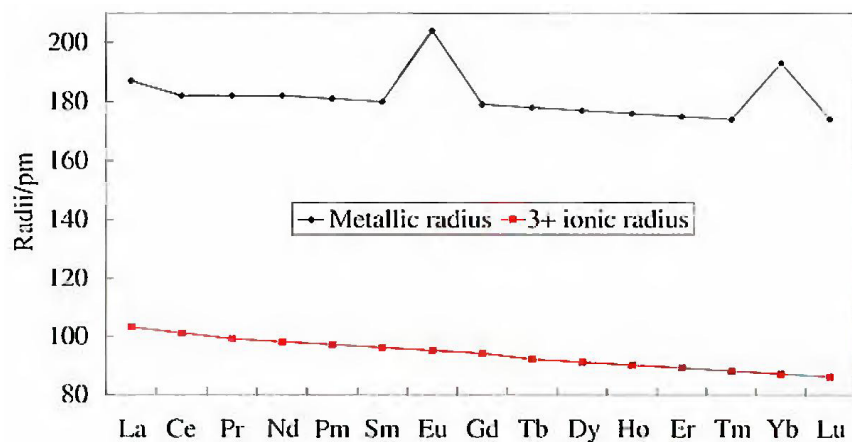


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Chemical element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Image															
Density (g/cm <sup>3</sup> )	6.162	6.770	6.77	7.01	7.26	7.52	5.244	7.90	8.23	8.540	8.79	9.066	9.32	6.90	9.841
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 <sup>1</sup>	4f <sup>1</sup> 5d <sup>1</sup>	4f <sup>3</sup>	4f <sup>4</sup>	4f <sup>5</sup>	4f <sup>6</sup>	4f <sup>7</sup>	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>9</sup>	4f <sup>10</sup>	4f <sup>11</sup>	4f <sup>12</sup>	4f <sup>13</sup>	4f <sup>14</sup>	4f <sup>14</sup> 5d <sup>1</sup>
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 <sub>mol</sub> /10 <sup>-6</sup> (cm <sup>3</sup> ·mol <sup>-1</sup> )	+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<sup>2</sup> electronic shells



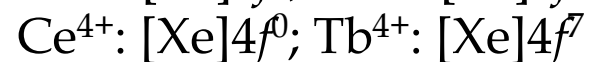
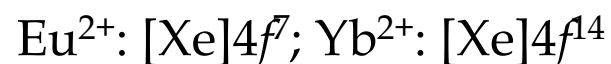


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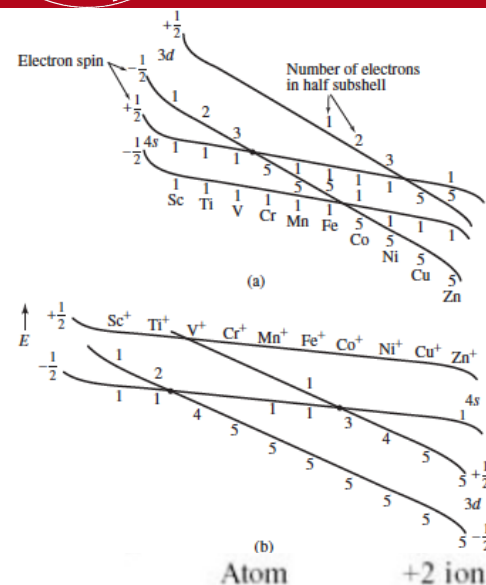
# Chimica Inorganica 3

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 <sup>3</sup> )	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 <sup>1</sup>	4f <sup>1</sup> 5d <sup>1</sup>	4f <sup>3</sup>	4f <sup>4</sup>	4f <sup>5</sup>	4f <sup>6</sup>	4f <sup>7</sup>	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>9</sup>	4f <sup>10</sup>	4f <sup>11</sup>	4f <sup>12</sup>	4f <sup>13</sup>	4f <sup>14</sup>	4f <sup>14</sup> 5d <sup>1</sup>
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 <sub>mol</sub> /10 <sup>-6</sup> (cm <sup>3</sup> ·mol <sup>-1</sup> )	+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<sup>2</sup> electronic shells



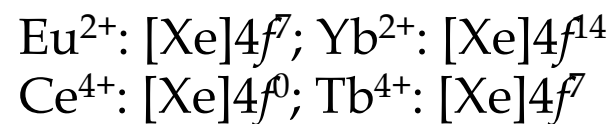
Chemical element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ln <sup>3+</sup> electron configuration*[ <sup>10</sup> ]	4f <sup>0</sup>	4f <sup>1</sup>	4f <sup>2</sup>	4f <sup>3</sup>	4f <sup>4</sup>	4f <sup>5</sup>	4f <sup>6</sup>	4f <sup>7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



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

## 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.



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 <sup>3+</sup> electron configuration* <sup>[10]</sup>	4f <sup>0</sup>	4f <sup>1</sup>	4f <sup>2</sup>	4f <sup>3</sup>	4f <sup>4</sup>	4f <sup>5</sup>	4f <sup>6</sup>	4f <sup>7</sup>	4f <sup>8</sup>	4f <sup>9</sup>	4f <sup>10</sup>	4f <sup>11</sup>	4f <sup>12</sup>	4f <sup>13</sup>	4f <sup>14</sup>
Ln <sup>3+</sup> radius (pm) <sup>[8]</sup>	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 <sup>4+</sup> ion colour in aqueous solution <sup>[11]</sup>	—	Orange-yellow	Yellow	Blue-violet	—	—	—	—	Red-brown	Orange-yellow	—	—	—	—	—
Ln <sup>3+</sup> ion colour in aqueous solution <sup>[10]</sup>	Colorless	Colorless	Green	Violet	Pink	Pale yellow	Colorless	Colorless	V. pale pink	Pale yellow	Yellow	Rose	Pale green	Colorless	Colorless
Ln <sup>2+</sup> ion colour in aqueous solution <sup>[8]</sup>	—	—	—	—	—	Blood red	Colorless	—	—	—	—	—	Violet-red	Yellow-green	—





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

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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PERIODIC TABLE  
Atomic Properties of the Elements

Frequently used fundamental physical constants  
For the most accurate values of these and other constants, visit [physics.nist.gov/constants](http://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  $^{133}\text{Cs}$

speed of light in vacuum  $c$  299 792 458 m s $^{-1}$  (exact)  
Planck constant  $h$  6.626 07  $\times 10^{-34}$  J s  
elementary charge  $e$  1.602 177  $\times 10^{-19}$  C  
electron mass  $m_e$  9.109 38  $\times 10^{-31}$  kg  
 $m_p/m_e$  1.836 152 673 43  
proton mass 1.672 622  $\times 10^{-27}$  kg  
fine-structure constant  $\alpha$  7.297 352 569 3  
Rydberg constant  $R_\infty$  10 973 731.568 1 m $^{-1}$   
 $R_H$  1.097 373 156 85  $\times 10^7$  m $^{-1}$   
 $R_\infty hc$  13.605 69 eV  
Boltzmann constant  $k$  1.380 65  $\times 10^{-23}$  J K $^{-1}$

Physical Measurement Laboratory  
Standard Reference Data

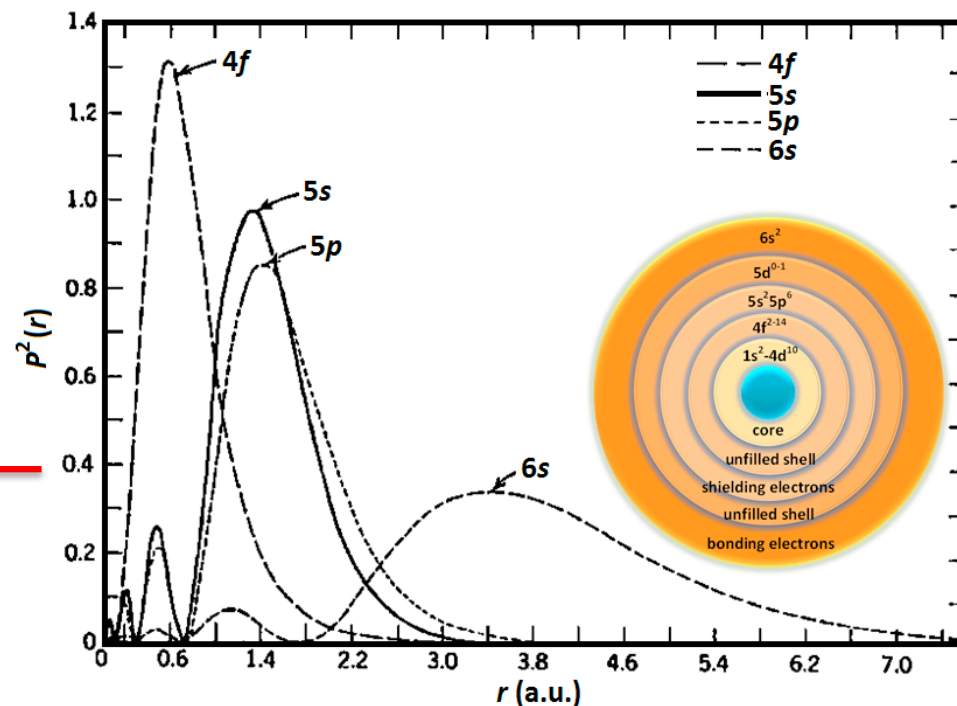
50 elements are shaded to indicate their physical state at standard conditions: Solids (blue), Liquids (red), Gases (green), Artificially Prepared (yellow).

Atomic Number, Symbol, Name, Standard Atomic Weight, Ground-state Configuration, Ionization Energy (eV)

Based upon  $^{12}\text{C}$ . ( ) indicates the mass number of the longest-lived isotope.

<sup>1</sup>UPAC conventional atomic weights; standard atomic weights for these elements are expressed in intervals; see [iupac.org](http://iupac.org) for an explanation and values.

NIST SP 966 (September 2014)



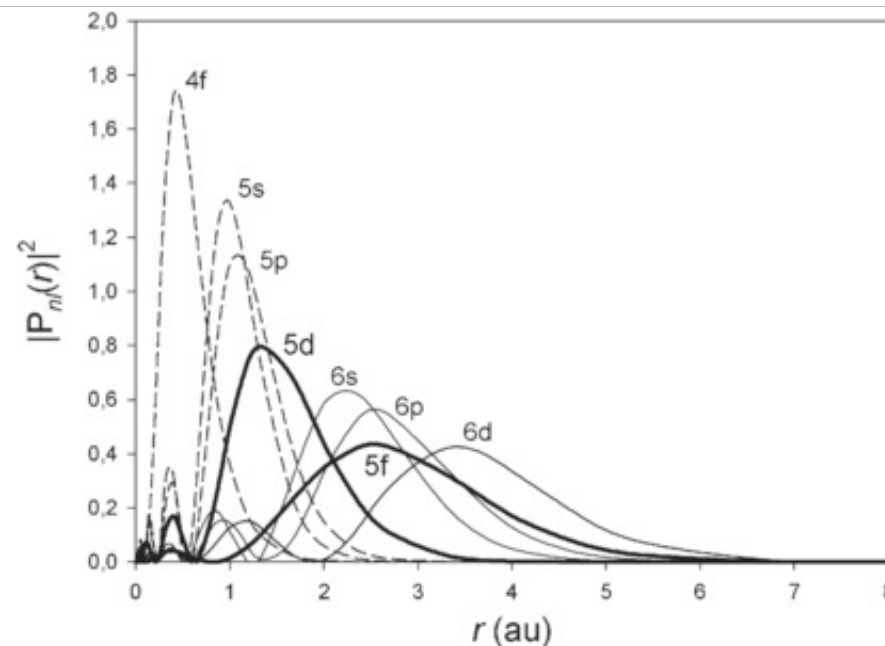
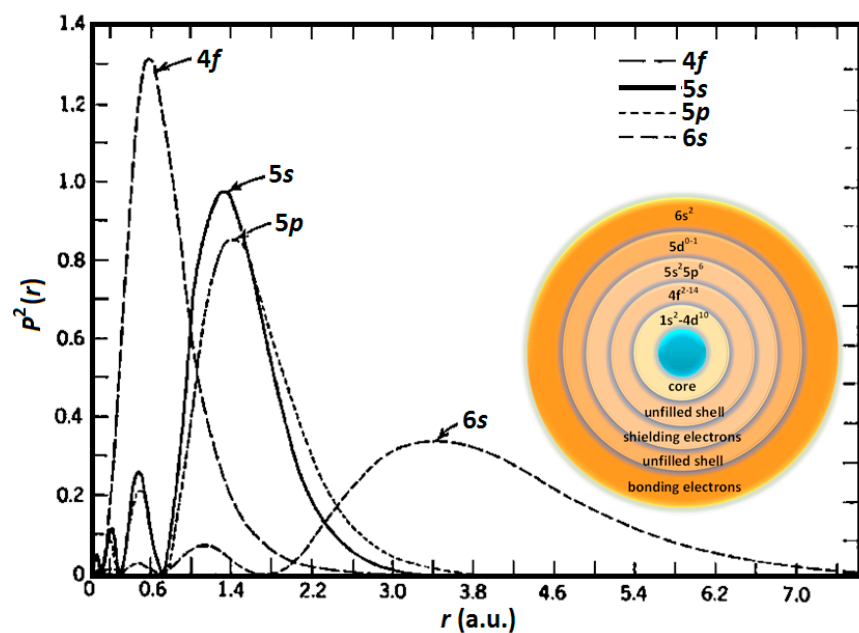
The  $4f$   $e^-$  of the lanthanide element ions are shielded from the perturbing effects of ligands by outer lying  $s$  and  $p$   $e^-$ . This shielding accounts for the great similarity of the chemical properties of lanthanide compounds, it also explains the evidence that the magnitude of their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



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The diagram illustrates the filling order of atomic orbitals (AOs) according to the Aufbau principle. On the left, a triangular diagram shows the sequence of orbitals filled, with arrows indicating the direction of increasing energy. The orbitals are labeled as follows:

- 1s<sup>2</sup>
- 2s<sup>2</sup>, 2p<sup>6</sup>
- 3s<sup>2</sup>, 3p<sup>6</sup>
- 4s<sup>2</sup>, 3d<sup>10</sup>
- 5s<sup>2</sup>, 4d<sup>10</sup>
- 6s<sup>2</sup>, 4f<sup>14</sup>, 5d<sup>10</sup>
- 7s<sup>2</sup>, 5f<sup>14</sup>, 6d<sup>10</sup>
- 8s<sup>2</sup>, 6f<sup>14</sup>, 7d<sup>10</sup>
- 9s<sup>2</sup>, 7f<sup>14</sup>, 8d<sup>10</sup>
- 10s<sup>2</sup>, 8f<sup>14</sup>, 9d<sup>10</sup>
- 11s<sup>2</sup>, 9f<sup>14</sup>, 10d<sup>10</sup>
- 12s<sup>2</sup>, 10f<sup>14</sup>, 11d<sup>10</sup>
- 13s<sup>2</sup>, 11f<sup>14</sup>, 12d<sup>10</sup>
- 14s<sup>2</sup>, 12f<sup>14</sup>, 13d<sup>10</sup>
- 15s<sup>2</sup>, 13f<sup>14</sup>, 14d<sup>10</sup>
- 16s<sup>2</sup>, 14f<sup>14</sup>, 15d<sup>10</sup>
- 17s<sup>2</sup>, 15f<sup>14</sup>, 16d<sup>10</sup>
- 18s<sup>2</sup>, 16f<sup>14</sup>, 17d<sup>10</sup>
- 19s<sup>2</sup>, 17f<sup>14</sup>, 18d<sup>10</sup>
- 20s<sup>2</sup>, 18f<sup>14</sup>, 19d<sup>10</sup>
- 21s<sup>2</sup>, 19f<sup>14</sup>, 20d<sup>10</sup>
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- 24s<sup>2</sup>, 22f<sup>14</sup>, 23d<sup>10</sup>
- 25s<sup>2</sup>, 23f<sup>14</sup>, 24d<sup>10</sup>
- 26s<sup>2</sup>, 24f<sup>14</sup>, 25d<sup>10</sup>
- 27s<sup>2</sup>, 25f<sup>14</sup>, 26d<sup>10</sup>
- 28s<sup>2</sup>, 26f<sup>14</sup>, 27d<sup>10</sup>
- 29s<sup>2</sup>, 27f<sup>14</sup>, 28d<sup>10</sup>
- 30s<sup>2</sup>, 28f<sup>14</sup>, 29d<sup>10</sup>
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- 106s<sup>2</sup>





# Chimica Inorganica 3

$$\begin{aligned} Y_3^{-3}(\theta, \varphi) &= \frac{1}{8} \sqrt{\frac{35}{\pi}} \cdot e^{-3i\varphi} \cdot \sin^3 \theta = \frac{1}{8} \sqrt{\frac{35}{\pi}} \cdot \frac{(x - iy)^3}{r^3} \\ Y_3^{-2}(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{105}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2 \theta \cdot \cos \theta = \frac{1}{4} \sqrt{\frac{105}{2\pi}} \cdot \frac{(x - iy)^2 z}{r^3} \\ Y_3^{-1}(\theta, \varphi) &= \frac{1}{8} \sqrt{\frac{21}{\pi}} \cdot e^{-i\varphi} \cdot \sin \theta \cdot (5 \cos^2 \theta - 1) = \frac{1}{8} \sqrt{\frac{21}{\pi}} \cdot \frac{(x - iy)(4z^2 - x^2 - y^2)}{r^3} \\ Y_3^0(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{7}{\pi}} \cdot (5 \cos^3 \theta - 3 \cos \theta) = \frac{1}{4} \sqrt{\frac{7}{\pi}} \cdot \frac{z(2z^2 - 3x^2 - 3y^2)}{r^3} \\ Y_3^1(\theta, \varphi) &= \frac{-1}{8} \sqrt{\frac{21}{\pi}} \cdot e^{i\varphi} \cdot \sin \theta \cdot (5 \cos^2 \theta - 1) = \frac{-1}{8} \sqrt{\frac{21}{\pi}} \cdot \frac{(x + iy)(4z^2 - x^2 - y^2)}{r^3} \\ Y_3^2(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{105}{2\pi}} \cdot e^{2i\varphi} \cdot \sin^2 \theta \cdot \cos \theta = \frac{1}{4} \sqrt{\frac{105}{2\pi}} \cdot \frac{(x + iy)^2 z}{r^3} \\ Y_3^3(\theta, \varphi) &= \frac{-1}{8} \sqrt{\frac{35}{\pi}} \cdot e^{3i\varphi} \cdot \sin^3 \theta = \frac{-1}{8} \sqrt{\frac{35}{\pi}} \cdot \frac{(x + iy)^3}{r^3} \end{aligned}$$

$$\begin{aligned} Y_{3,-3} &= f_{y(3x^2-y^2)} = i\sqrt{\frac{1}{2}} (Y_3^{-3} + Y_3^3) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{(3x^2 - y^2)y}{r^3} \\ Y_{3,-2} &= f_{xyz} = i\sqrt{\frac{1}{2}} (Y_3^{-2} - Y_3^2) = \frac{1}{2}\sqrt{\frac{105}{\pi}} \cdot \frac{xyz}{r^3} \\ Y_{3,-1} &= f_{yz^2} = i\sqrt{\frac{1}{2}} (Y_3^{-1} + Y_3^1) = \frac{1}{4}\sqrt{\frac{21}{2\pi}} \cdot \frac{y(4z^2 - x^2 - y^2)}{r^3} \\ Y_{30} &= f_{z^3} = Y_3^0 = \frac{1}{4}\sqrt{\frac{7}{\pi}} \cdot \frac{z(2z^2 - 3x^2 - 3y^2)}{r^3} \\ Y_{31} &= f_{xz^2} = \sqrt{\frac{1}{2}} (Y_3^{-1} - Y_3^1) = \frac{1}{4}\sqrt{\frac{21}{2\pi}} \cdot \frac{x(4z^2 - x^2 - y^2)}{r^3} \\ Y_{32} &= f_{z(x^2-y^2)} = \sqrt{\frac{1}{2}} (Y_3^{-2} + Y_3^2) = \frac{1}{4}\sqrt{\frac{105}{\pi}} \cdot \frac{(x^2 - y^2)z}{r^3} \\ Y_{33} &= f_{x(x^2-3y^2)} = \sqrt{\frac{1}{2}} (Y_3^{-3} - Y_3^3) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{(x^2 - 3y^2)x}{r^3} \end{aligned}$$



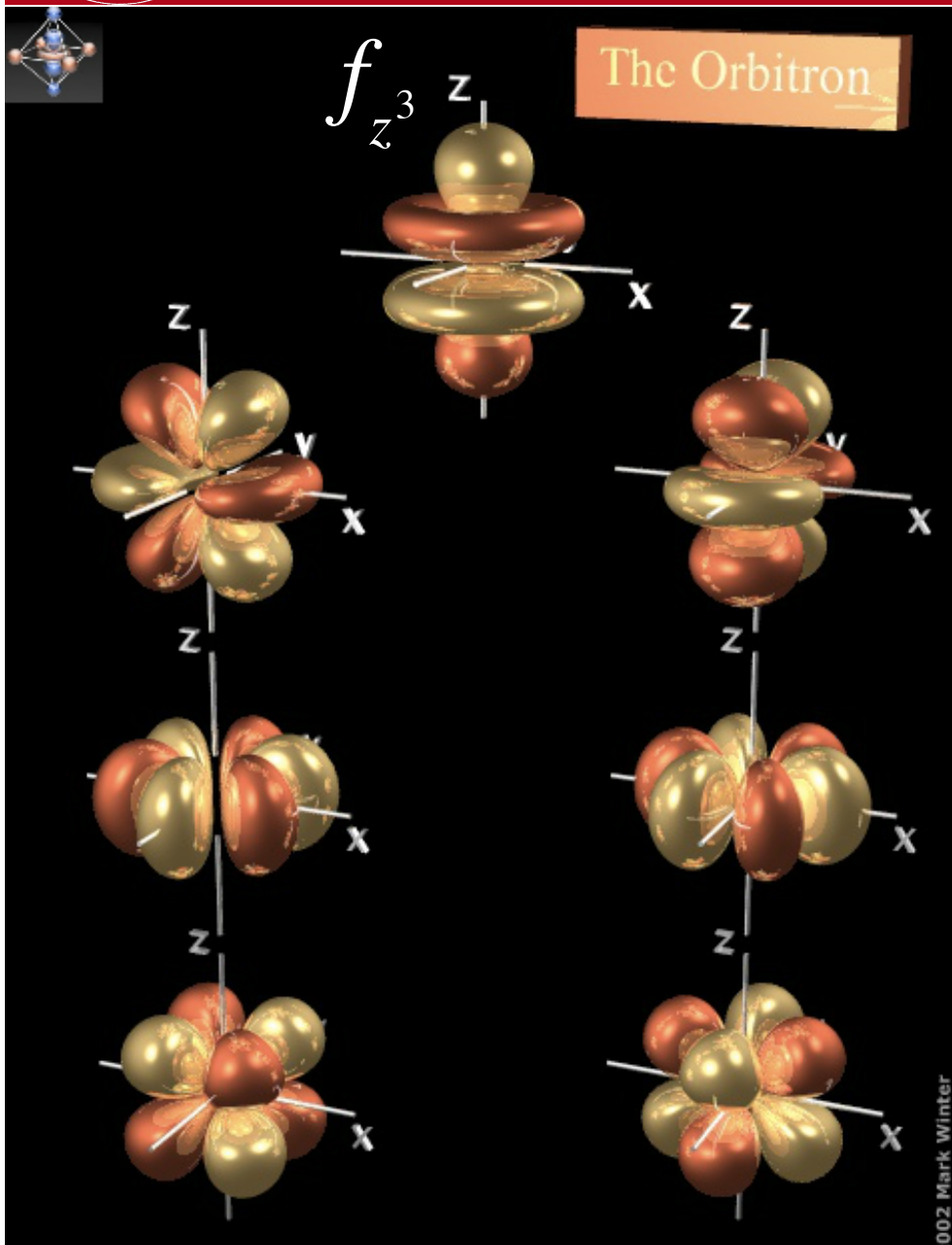


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# Chimica Inorganica 3

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

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



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



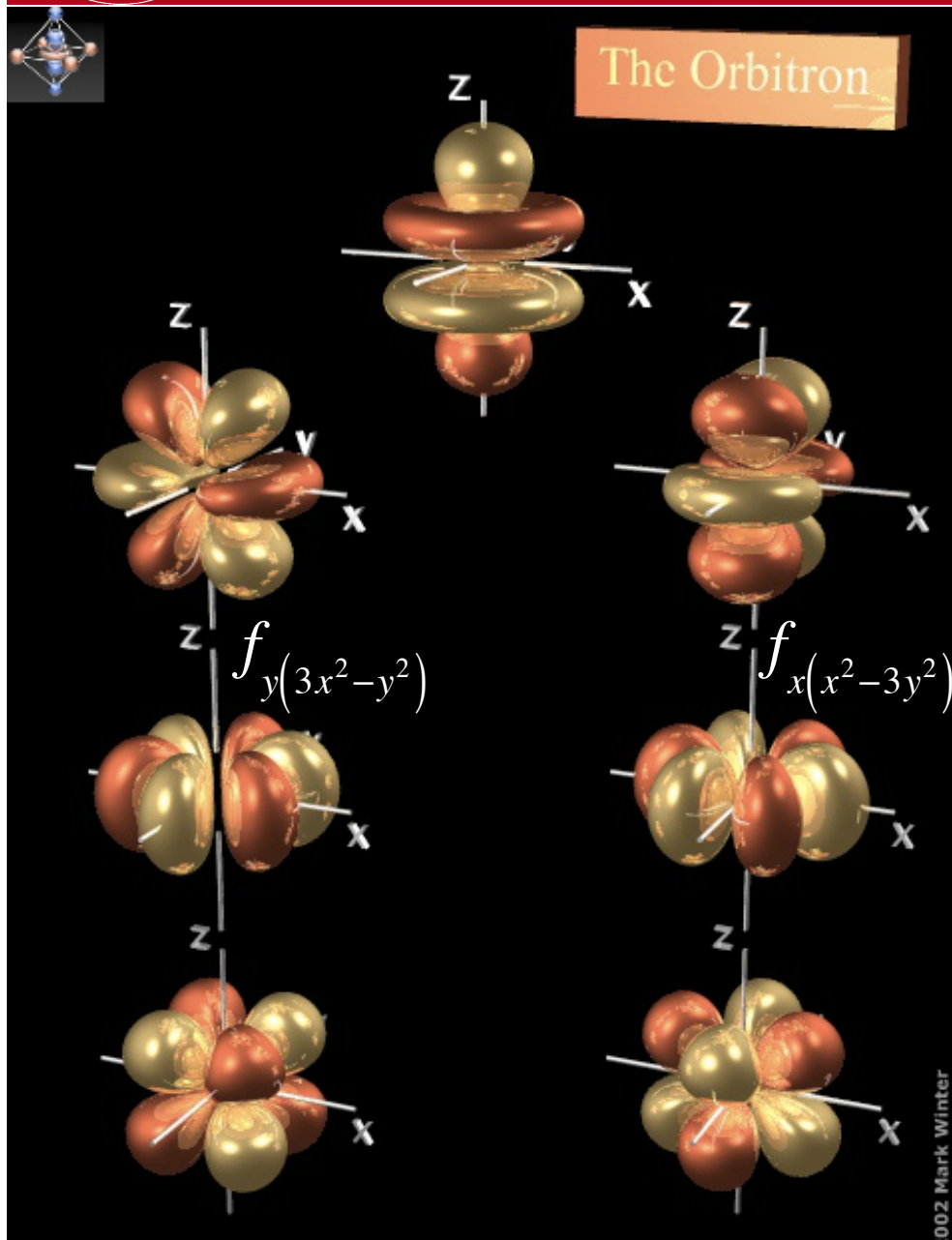


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$$Y_{33} = f_{x(x^2-3y^2)} = \sqrt{\frac{1}{2}} (Y_3^{-3} - Y_3^3) = \frac{1}{4}\sqrt{\frac{35}{2\pi}} \cdot \frac{(x^2 - 3y^2) x}{r^3}$$

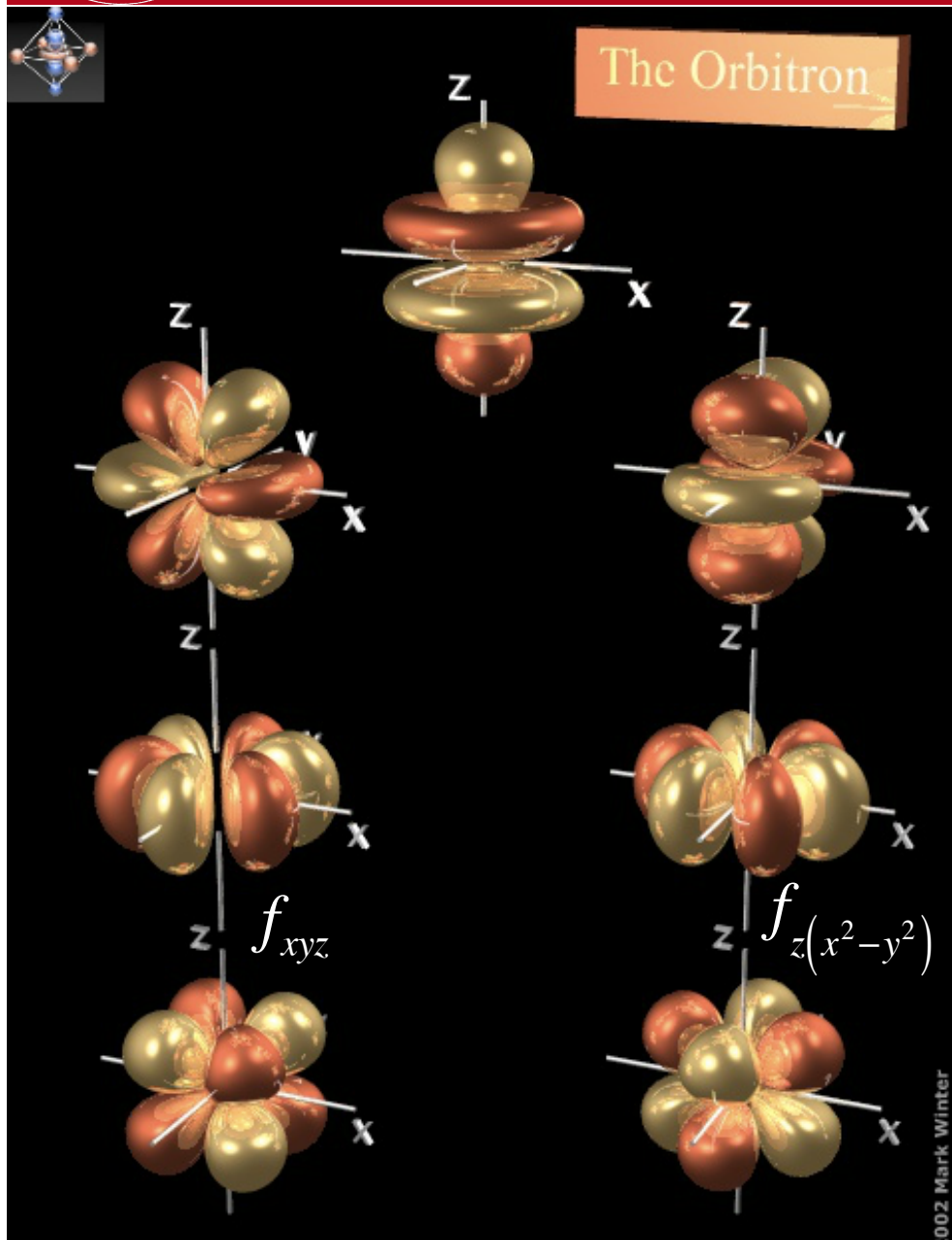


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$$Y_{3,-2} = f_{xyz} = i\sqrt{\frac{1}{2}} (Y_3^{-2} - Y_3^2) = \frac{1}{2} \sqrt{\frac{105}{\pi}} \cdot \frac{xyz}{r^3}$$

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





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# Chimica Inorganica 3

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

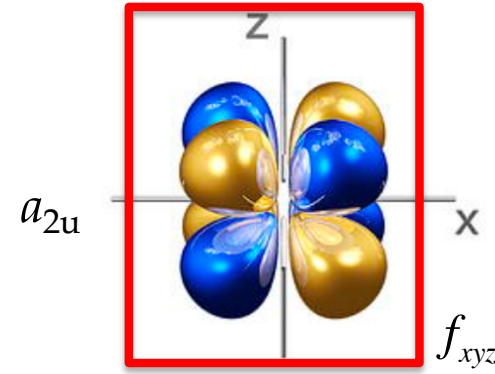
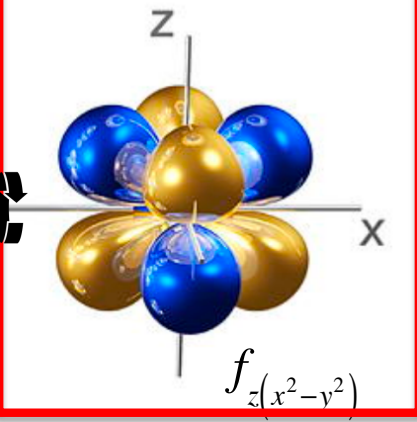
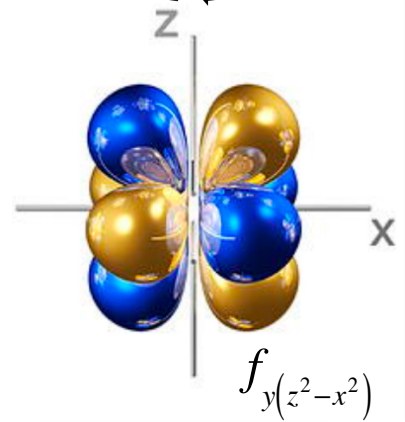
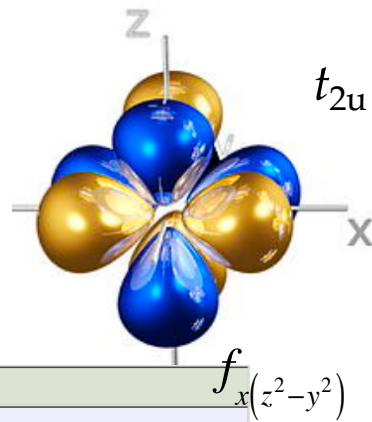
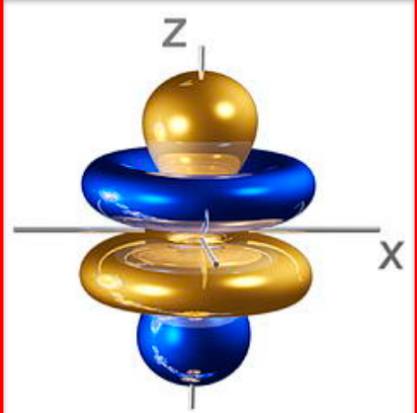
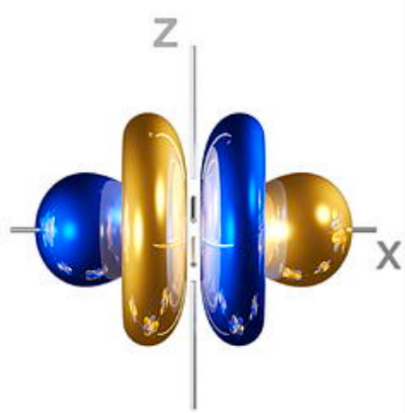
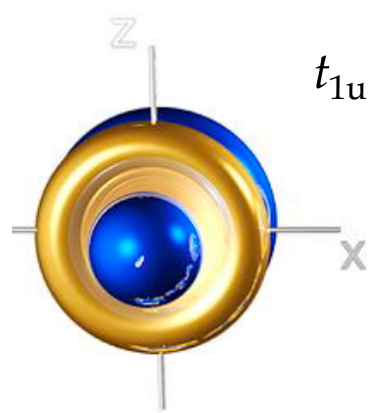
$$R_{43}(r) = \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\rho_n}{2}} \frac{1}{96\sqrt{35}} \rho_n^3$$

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

$$f_{z(x^2-y^2)} = f_{z(x^2-y^2)}$$

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

$$a_{2u} : \begin{cases} f_{xyz} = f_{xyz} \end{cases}$$



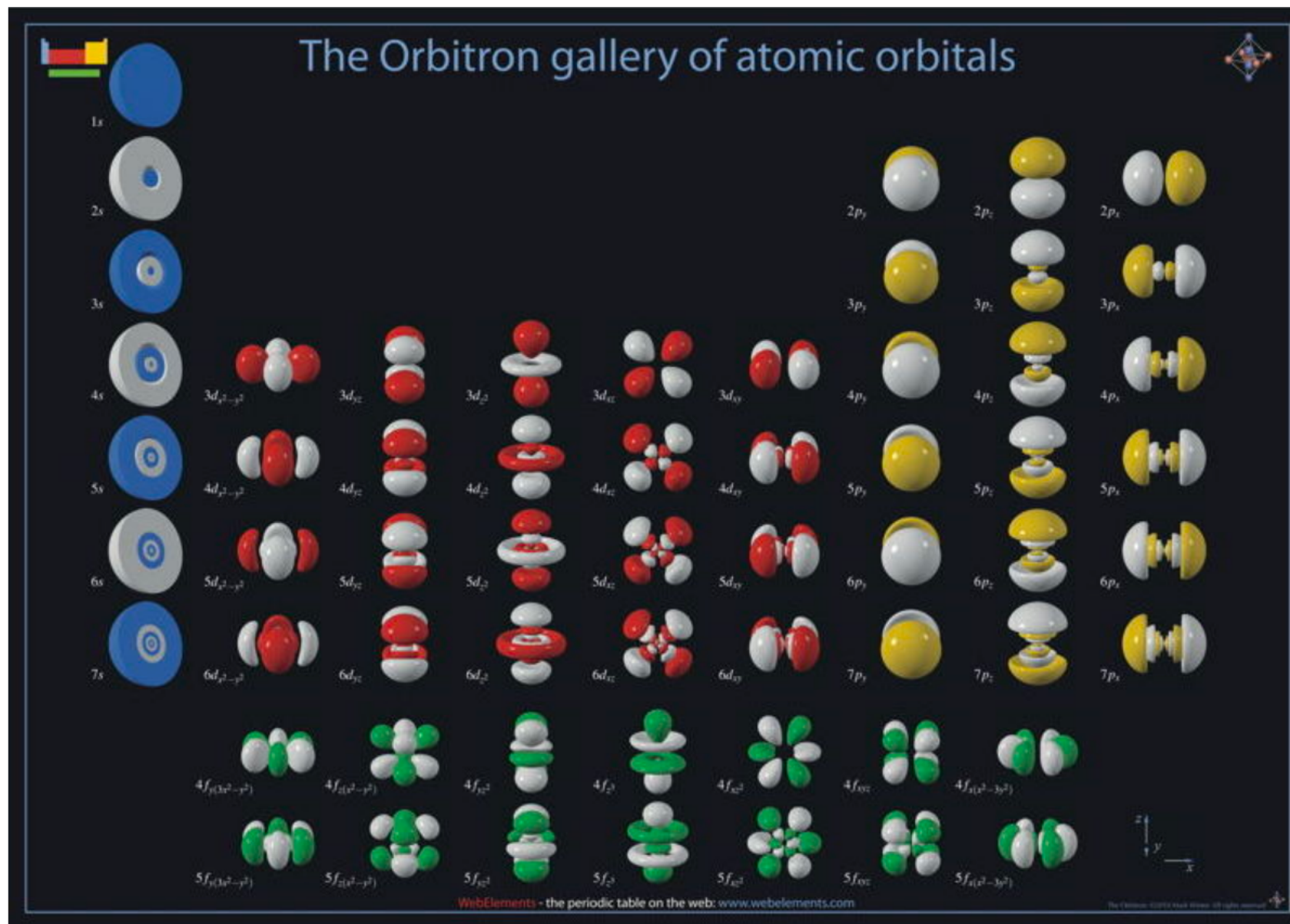
O <sub>h</sub>	E	8C <sub>3</sub>	6C <sub>2</sub>	6C <sub>4</sub>	3C <sub>2'</sub>	i	6S <sub>4</sub>	8S <sub>6</sub>	3σ <sub>h</sub>	6σ <sub>d</sub>	Cubic
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	
A <sub>2g</sub>	1	1	-1	-1	1	1	-1	1	1	-1	
E <sub>g</sub>	2	-1	0	0	2	2	0	-1	2	0	
T <sub>1g</sub>	3	0	-1	1	-1	3	1	0	-1	-1	
T <sub>2g</sub>	3	0	1	-1	-1	3	-1	0	-1	1	
A <sub>1u</sub>	1	1	1	1	1	-1	-1	-1	-1	-1	
A <sub>2u</sub>	1	1	-1	-1	1	-1	1	-1	-1	1	xyz
E <sub>u</sub>	2	-1	0	0	2	-2	0	1	-2	0	
T <sub>1u</sub>	3	0	-1	1	-1	-3	-1	0	1	1	(x <sup>3</sup> , y <sup>3</sup> , z <sup>3</sup> ); [x(z <sup>2</sup> +y <sup>2</sup> ), y(z <sup>2</sup> +x <sup>2</sup> ), z(x <sup>2</sup> +y <sup>2</sup> )]
T <sub>2u</sub>	3	0	1	-1	-1	-3	1	0	1	-1	[x(y <sup>2</sup> -z <sup>2</sup> ), z(x <sup>2</sup> -y <sup>2</sup> ), y(z <sup>2</sup> -x <sup>2</sup> )]



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



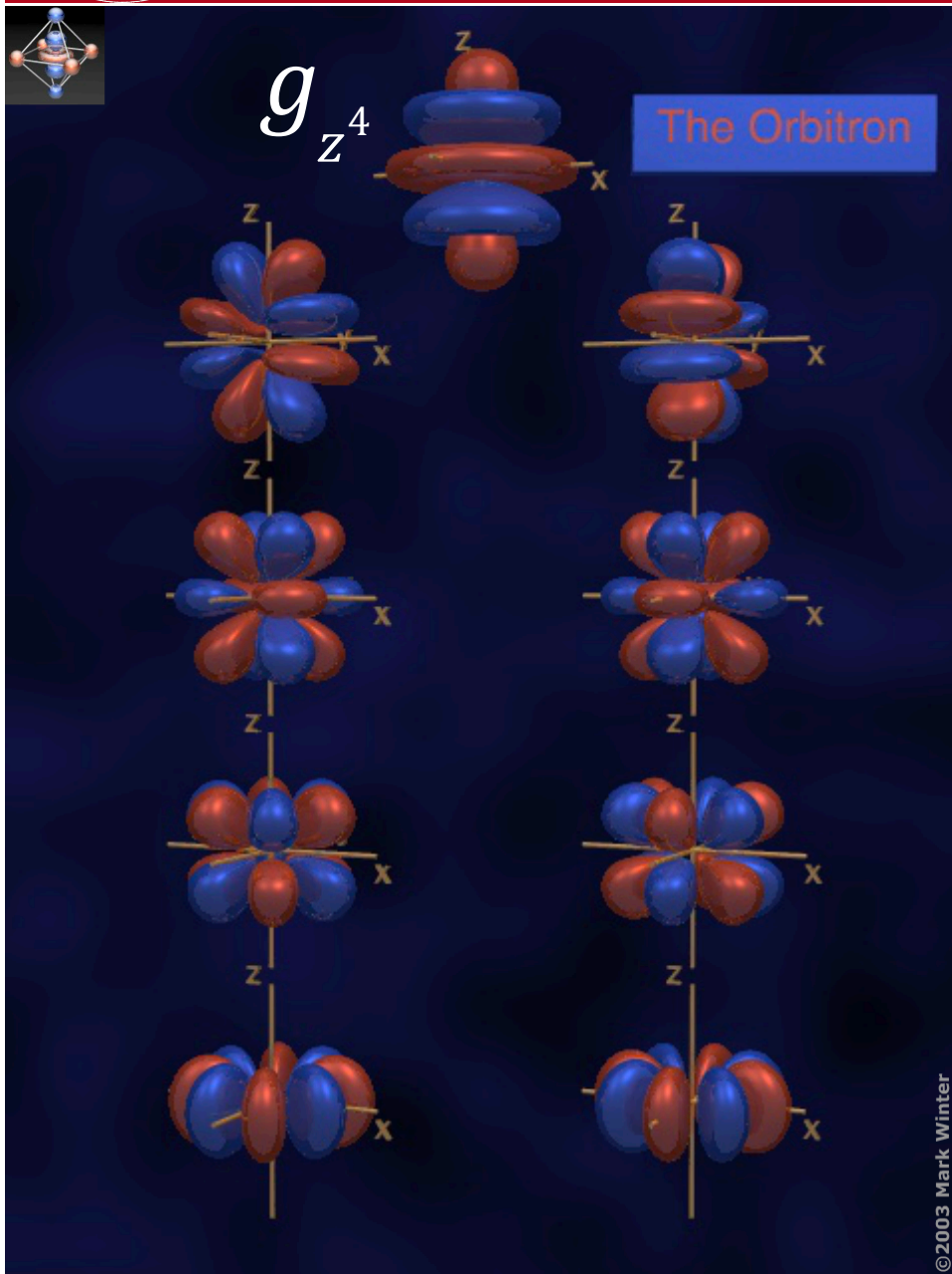


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# Chimica Inorganica 3

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

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



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

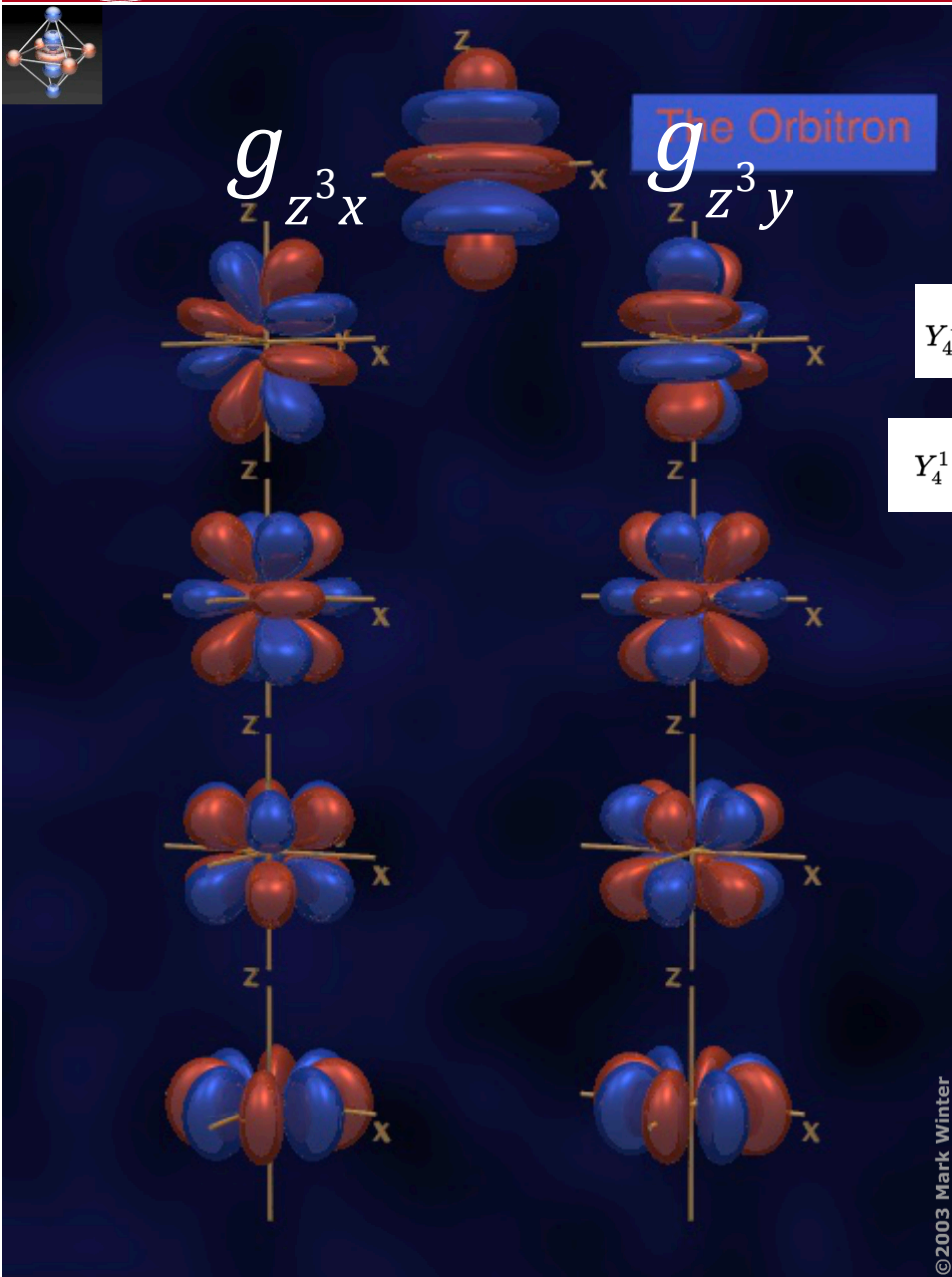


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$$Y_4^{-1}(\theta, \varphi) = \frac{3}{8} \sqrt{\frac{5}{\pi}} \cdot e^{-i\varphi} \cdot \sin \theta \cdot (7 \cos^3 \theta - 3 \cos \theta) = \frac{3}{8} \sqrt{\frac{5}{\pi}} \cdot \frac{(x - iy) \cdot z \cdot (7z^2 - 3r^2)}{r^4}$$

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



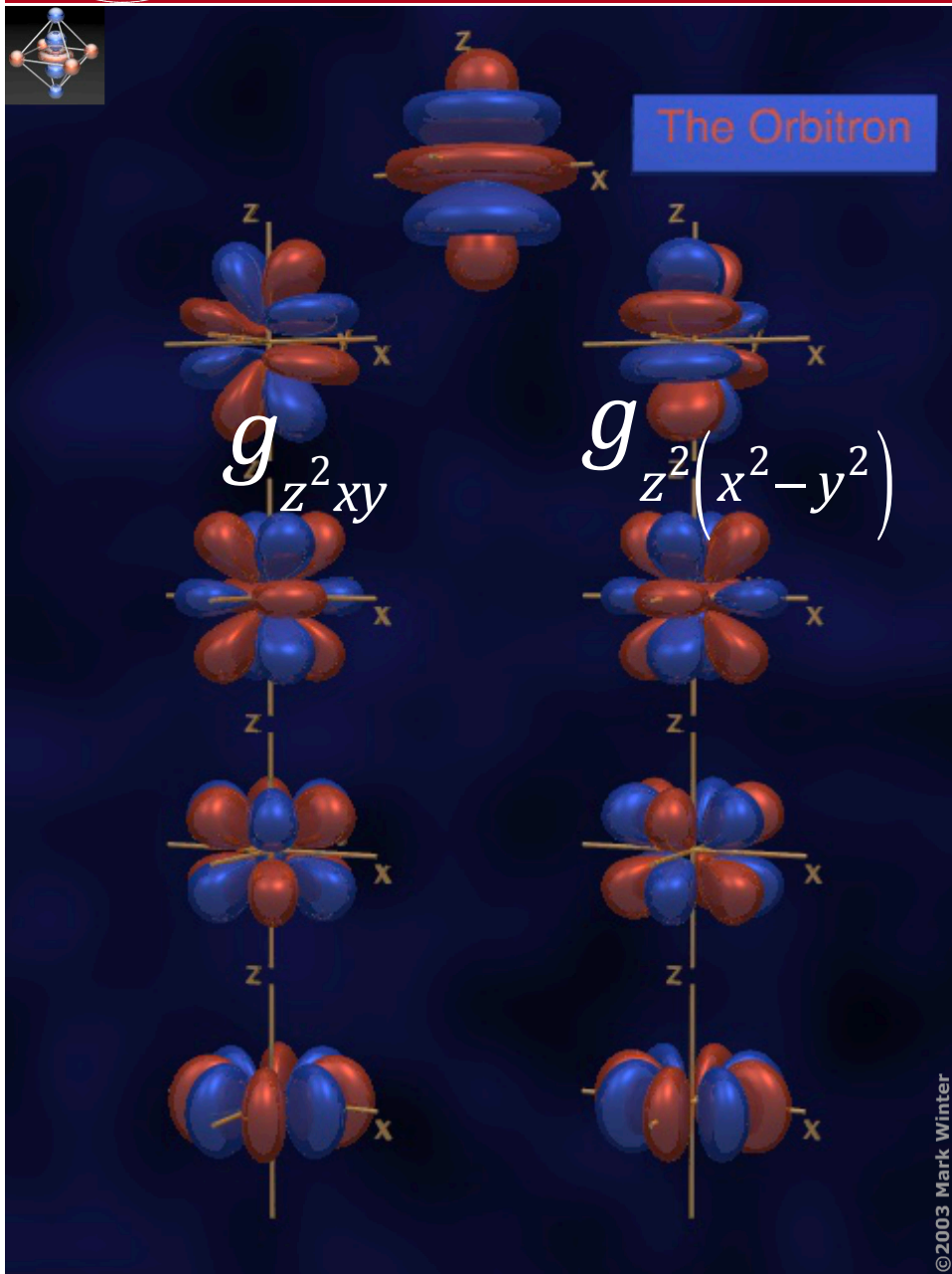


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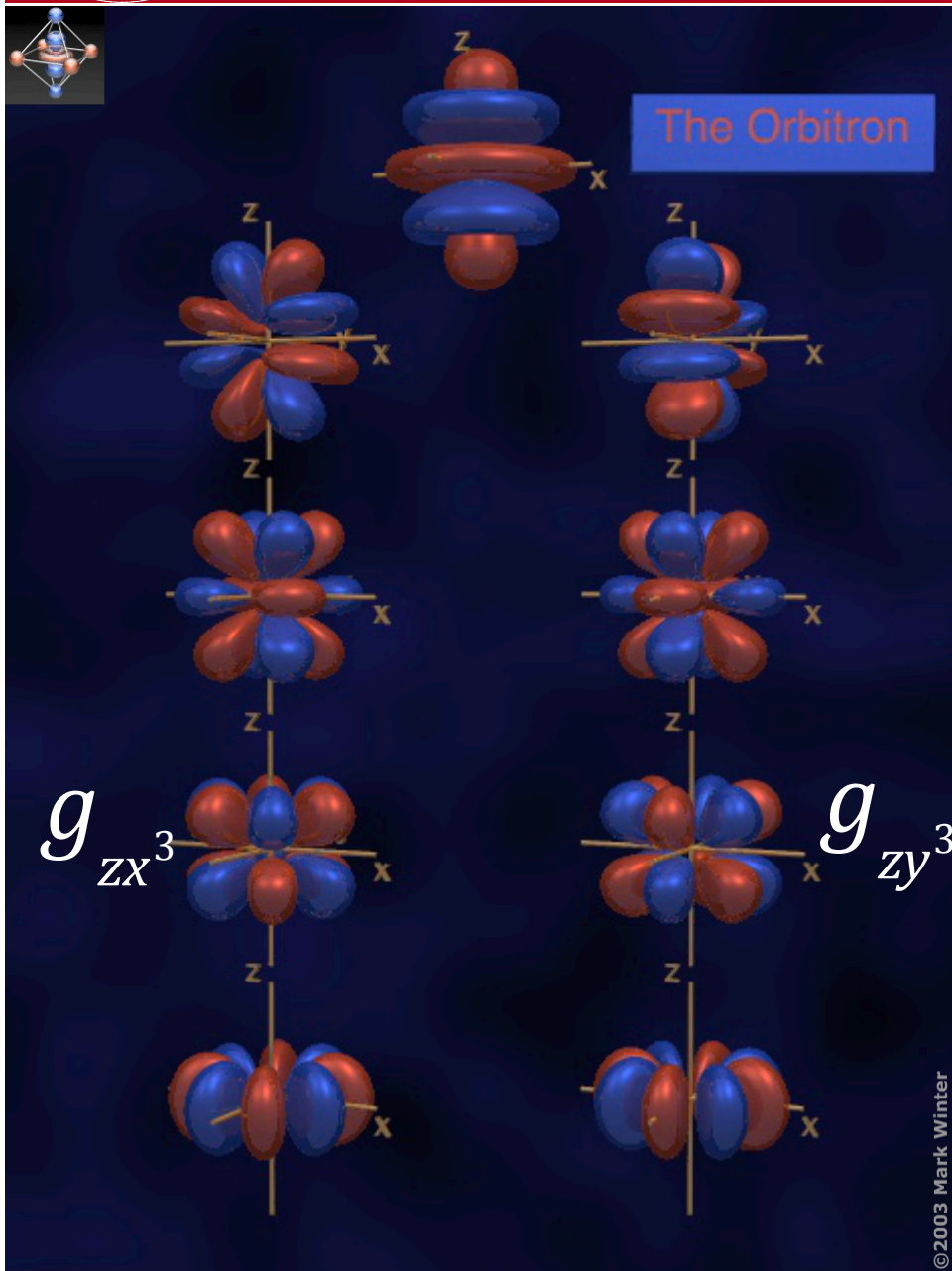


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$$Y_4^3(\theta, \varphi) = \frac{-3}{8} \sqrt{\frac{35}{\pi}} \cdot e^{3i\varphi} \cdot \sin^3 \theta \cdot \cos \theta = \frac{-3}{8} \sqrt{\frac{35}{\pi}} \cdot \frac{(x + iy)^3 z}{r^4}$$

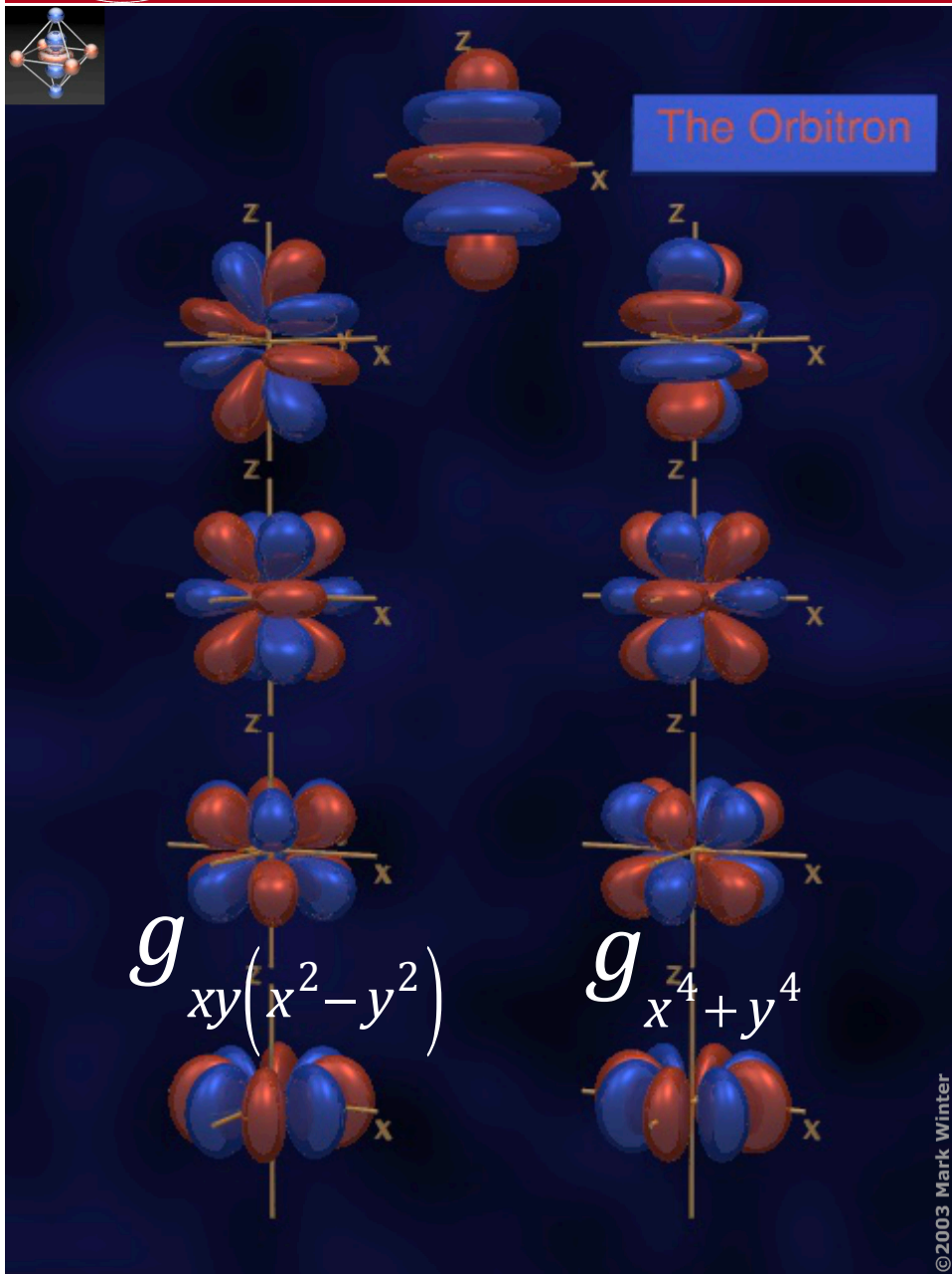


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# Chimica Inorganica 3

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



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# *Chimica Inorganica 3*

$\ell = 0$  (s)

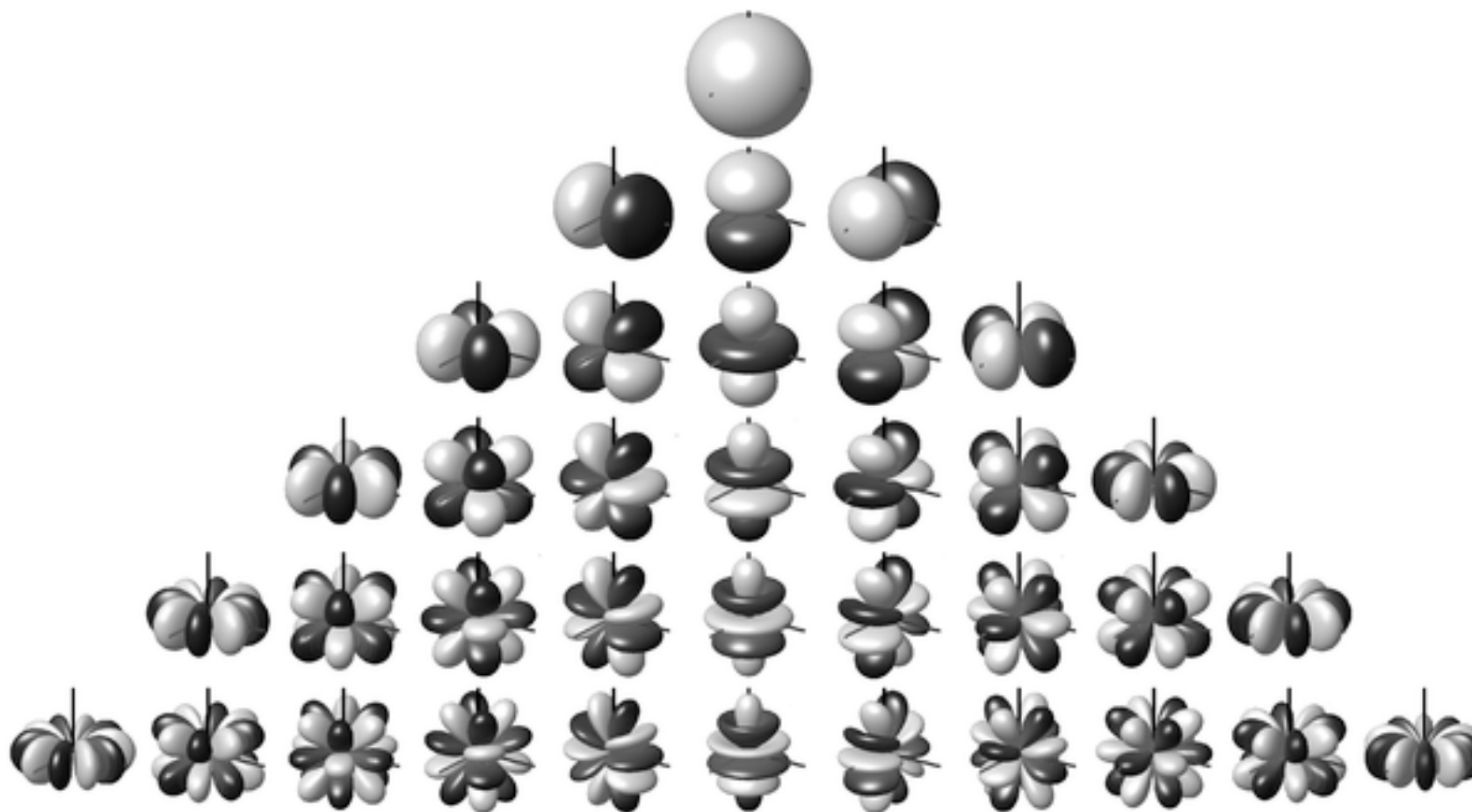
$\ell = 1$  (p)

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

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<sup>1</sup>**

$$\begin{aligned}\ell_1 &= 3 \\ L &= \ell_1 \\ L &= 3 \\ \text{F}\end{aligned}$$

$$\begin{aligned}s_1 &= 1/2 \\ S &= s_1 \\ 2S+1 &= 2\end{aligned}$$

$m_\ell \backslash m_s$	$1/2$	$-1/2$
3	3 <sup>+</sup>	3 <sup>-</sup>
2	2 <sup>+</sup>	2 <sup>-</sup>
1	1 <sup>+</sup>	1 <sup>-</sup>
0	0 <sup>+</sup>	0 <sup>-</sup>
-3	-3 <sup>+</sup>	-3 <sup>-</sup>
-2	-2 <sup>+</sup>	-2 <sup>-</sup>
-1	-1 <sup>+</sup>	-1 <sup>-</sup>

**2F**

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

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

$r$  = radius

$\pi = 3.14159$  approximately

$e = 2.71828$  approximately

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

$\rho = 2Zr/a_0n$  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 <sup>III</sup>	f <sup>0</sup>	none	0	<sup>1</sup> S
Ce <sup>III</sup>	f <sup>1</sup>	3	3	<sup>2</sup> F
Pr <sup>III</sup>	f <sup>2</sup>	3, 2	5	<sup>3</sup> H
Nd <sup>III</sup>	f <sup>3</sup>	3, 2, 1	6	<sup>4</sup> I
Pm <sup>III</sup>	f <sup>4</sup>	3, 2, 1, 0	6	<sup>5</sup> I
Sm <sup>III</sup>	f <sup>5</sup>	3, 2, 1, 0, -1	5	<sup>6</sup> H
Eu <sup>III</sup>	f <sup>6</sup>	3, 2, 1, 0, -1, -2	3	<sup>7</sup> F
Gd <sup>III</sup>	f <sup>7</sup>	3, 2, 1, 0, -1, -2, -3	0	<sup>8</sup> S
Tb <sup>III</sup>	f <sup>8</sup>	3 <sup>a</sup>	3	<sup>7</sup> F
Dy <sup>III</sup>	f <sup>9</sup>	3, 2	5	<sup>6</sup> H
Ho <sup>III</sup>	f <sup>10</sup>	3, 2, 1	6	<sup>5</sup> I
Er <sup>III</sup>	f <sup>11</sup>	3, 2, 1, 0	6	<sup>4</sup> I
Tm <sup>III</sup>	f <sup>12</sup>	3, 2, 1, 0, -1	5	<sup>3</sup> H
Yb <sup>III</sup>	f <sup>13</sup>	3, 2, 1, 0, -1, -2	3	<sup>2</sup> F
Lu <sup>III</sup>	f <sup>14</sup>	3, 2, 1, 0, -1, -2, -3	0	<sup>1</sup> S

<sup>a</sup> From Tb<sup>III</sup> 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  $\alpha$  and  $\beta$ ) 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 ( $\alpha$  or  $\beta$ ) 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  $p_\alpha^1$  or  $p_\alpha^2$ ; D for  $d_\alpha^1$  or  $d_\alpha^4$ ; F for  $f_\alpha^1$  or  $f_\alpha^6$  etc.



## Partial Terms Arising from the Occupancy of a Single Spin Set<sup>a,b</sup>

	Orbital occupancy (electrons or holes)							
Orbital set	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<sup>c</sup></i> <i>HIKM</i>	<i>SD[2]FG[2]</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<sup>a,b</sup>

	Orbital occupancy (electrons or holes)							
Orbital set	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<sup>c</sup></i> <i>HIKM</i>	<i>SD[2]FG[2]</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.**



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

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

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



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$m_l = +2$	$+1$	$0$	$-1$	$-2$	$M_L = \sum m_l$	$M_S = \sum m_s$	Array for $d^2$			
/	/				3	$+1, 0, 0, -1$	4	1		
/		/			2	$+1, 0, 0, -1$	3	1	2	1
/			/		1	$+1, 0, 0, -1$	2	1	3	1
/				/	0	$+1, 0, 0, -1$	1	2	4	2
	/	/			1	$+1, 0, 0, -1$	0	2	5	2
	/		/		0	$+1, 0, 0, -1$	-1	2	4	2
		/	/	/	-1	$+1, 0, 0, -1$	-2	1	3	1
			/	/	-1	$+1, 0, 0, -1$	-3	1	2	1
				/	-2	$+1, 0, 0, -1$	-4	1		
				/	-3	$+1, 0, 0, -1$				
×					4	0	$M_S$	1	0	-1
	×				2	0				
		×			0	0				
			×		-2	0				
				×	-4	0				

Arrays for spectral terms contained in array for  $d^2$

$M_L$	4	1	$L = 4$ $S = 0$ term $^1G$	$M_L$	3	1	1	1	$L = 3$ $S = 1$ term $^3F$
	3	1			2	1	1	1	
	2	1			1	1	1	1	
	1	1			0	1	1	1	
	0	1			-1	1	1	1	
	-1	1			-2	1	1	1	
	-2	1			-3	1	1	1	
	-3	1							
	-4	1							
		0				1	0	-1	
		$M_S$							
$M_L$	2	1	$L = 2$ $S = 0$ term $^1D$	$M_L$	1	1	1	1	$L = 1$ $S = 1$ term $^3P$
	1	1			0	1	1	1	
	0	1			-1	1	1	1	
	-1	1							
	-2	1							
		0				1	0	-1	
		$M_S$							
$M_L$	0	1	$L = 0$ $S = 0$ term $^1S$	$M_L$	0	1			
		0							
		$M_S$							



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

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

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

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

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

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

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

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

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

$$P \times D = \textcolor{red}{F} + D + \textcolor{red}{P} \quad (2+1 \leq L \leq 2-1)$$

$$F \times D = H + G + F + D + P \quad (3+2 \leq L \leq 3-2)$$

$$d^3 \rightarrow \underbrace{\underbrace{{}^4F}_{28} + \underbrace{{}^4P}_{12} + \underbrace{{}^2H}_{22} + \underbrace{{}^2G}_{18} + \underbrace{{}^2F}_{14} + \underbrace{{}^2D}_{20} + \underbrace{{}^2P}_6}_{120}$$



## Allowed terms for $p$ and $d$ configuration

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





## Partial Terms Arising from the Occupancy of a Single Spin Set<sup>a,b</sup>

	Orbital occupancy (electrons or holes)									
Orbital set	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<sup>c</sup></i> <i>HIKM</i>	<i>SD[2]FG[2]</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.**



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# Chimica Inorganica 3

$M_S$					
	$+3/2$	$+1/2$	$-1/2$	$-3/2$	
$M_L$	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

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

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

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.

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

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  $\alpha$  or  $\beta$ )**

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 M</i> (84)	<i>SD</i> [2] <i>FG</i> [2] <i>HI</i> [2] <i>KL N</i> (126)

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