

MAGNETISM IN MATERIALS

Lecture 3: Crystal Field Effects

- ❖ orbitals
- ❖ octahedral environment
- ❖ high spin/low spin
- ❖ orbital quenching
- ❖ Jahn-Teller effect

	s ($l = 0$)	p ($l = 1$)			d ($l = 2$)					f ($l = 3$)						
	$m = 0$	$m = 0$	$m = -1$	$m = +1$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = -3$	$m = +3$
	s	p _z	p _x	p _y	d _{z²}	d _{xz}	d _{yz}	d _{xy}	d _{x²-y²}	f _{z³}	f _{xz²}	f _{yz²}	f _{xyz}	f _{z(x²-y²)}	f _{x(x²-3y²)}	f _{y(3x²-y²)}
$n = 1$																
$n = 2$																
$n = 3$																
$n = 4$																
$n = 5$										...	...	...	...	...	...	...
$n = 6$										...†	...	...†	...	...†	...*	...*
$n = 7$		...†	...†	...†	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*

bonding

magnetism

- ❖ based on hydrogen
- ❖ visualization is not straight-forward
- ❖ radial and spherical coordinates
- ❖ complex value

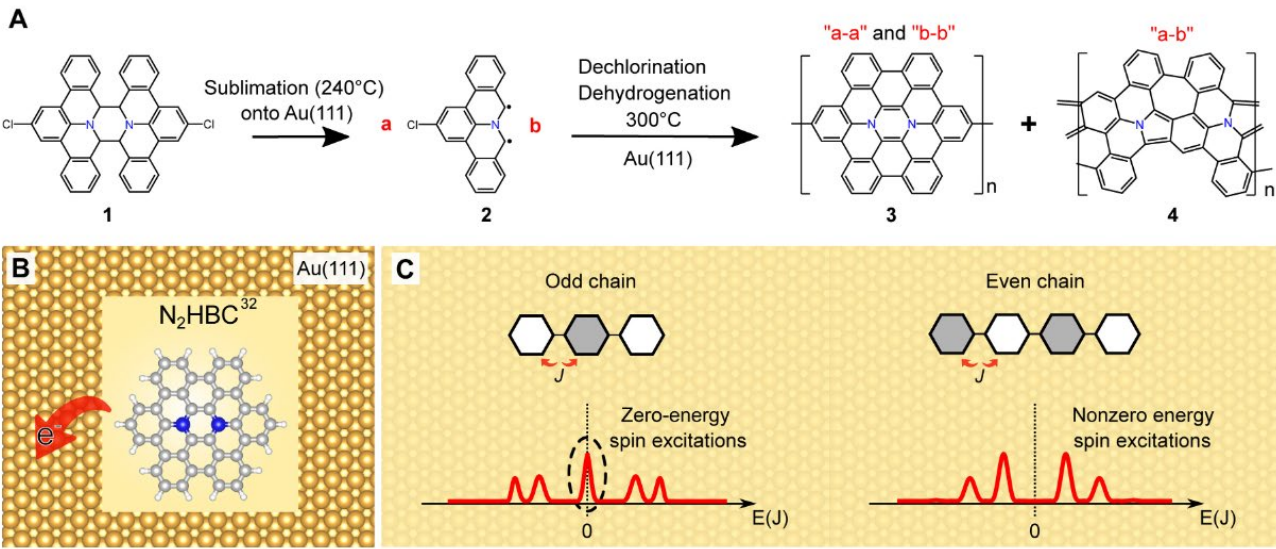
	s ($l = 0$)				p ($l = 1$)					d ($l = 2$)					f ($l = 3$)						
	$m = 0$	$m = 0$	$m = -1$	$m = +1$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = 0$	$m = -1$	$m = +1$	$m = -2$	$m = +2$	$m = -3$	$m = +3$					
	s	p _z	p _x	p _y	d _{z²}	d _{xz}	d _{yz}	d _{xy}	d _{x²-y²}	f _{z³}	f _{xz²}	f _{yz²}	f _{xyz}	f _{z(x²-y²)}	f _{x(x²-3y²)}	f _{y(3x²-y²)}					
$n = 1$																					
$n = 2$																					
$n = 3$																					
$n = 4$																					
$n = 5$										...	...	...	...	...	...	...					
$n = 6$					...†	...	...†	...	...†	...*	...*	...*	...*	...*	...*	...*					
$n = 7$		...†	...†	...†	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*					

- ❖ based on hydrogen
- ❖ visualization is not straight-forward
- ❖ radial and spherical coordinates
- ❖ complex value

bonding

magnetism

Sci. Adv.11,eads1641(2025)



	s (l = 0)				p (l = 1)					d (l = 2)					f (l = 3)						
	m = 0				m = 0	m = -1	m = +1	m = -1	m = +1	m = 0	m = -1	m = +1	m = -2	m = +2	m = 0	m = -1	m = +1	m = -2	m = +2	m = -3	m = +3
	s	p _z	p _x	p _y	d _{z²}	d _{xz}	d _{yz}	d _{xy}	d _{x²-y²}	f _{z³}	f _{xz²}	f _{yz²}	f _{xyz}	f _{z(x²-y²)}	f _{x(x²-3y²)}	f _{y(3x²-y²)}					
n = 1	•																				
n = 2	•																				
n = 3	•																				
n = 4																					
n = 5										...	...	...	...	...	...	...					
n = 6					...†	...	...†	...	...†	...*	...*	...*	...*	...*	...*	...*					
n = 7		...†	...†	...†	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*	...*					

- ❖ based on hydrogen
- ❖ radial and angular coordinates
- ❖ complex value
- ❖ visualization is not straight-forward

bonding

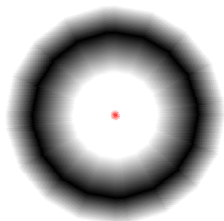
magnetism

$$p_0 = R_{n,l=1}Y_{l=1,m=0}$$
$$p_1 = R_{n,l=1}Y_{l=1,m=1}$$
$$p_{-1} = R_{n,l=1}Y_{l=1,m=-1}$$

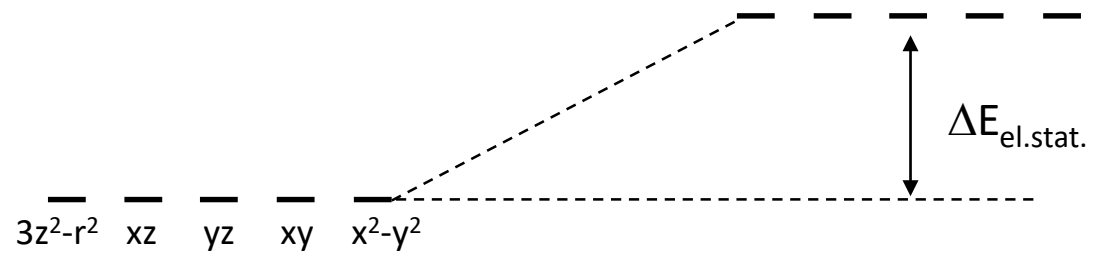
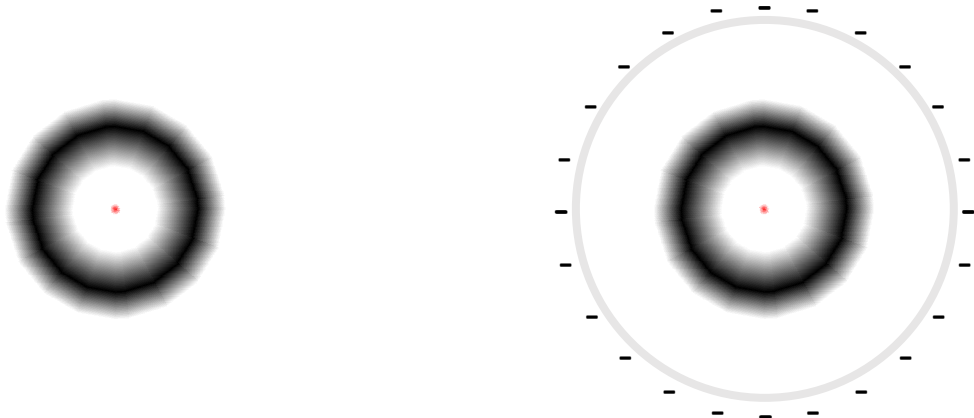
$$p_x = \frac{1}{\sqrt{2}}(-p_1 + p_{-1})$$
$$p_y = \frac{i}{\sqrt{2}}(p_1 + p_{-1})$$
$$p_z = p_0$$

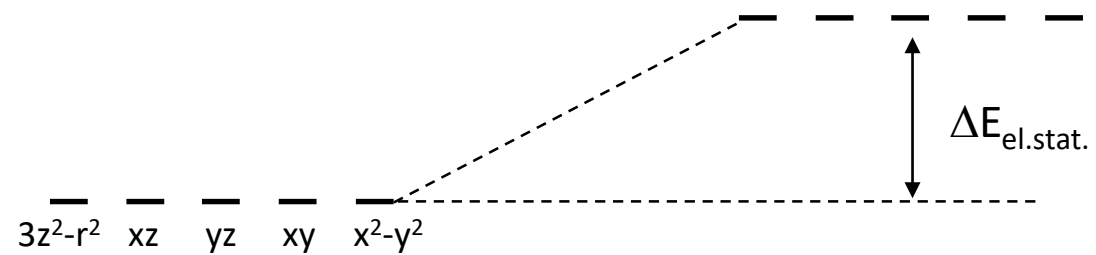
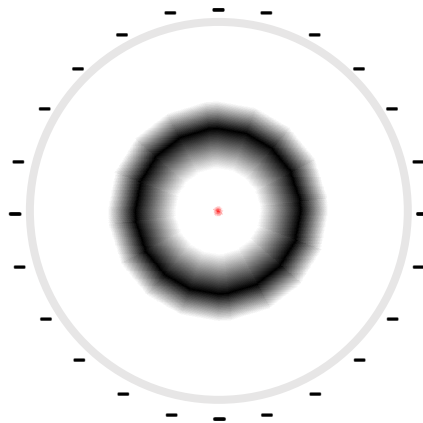
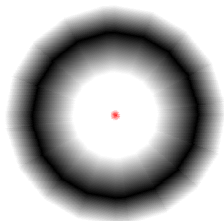
$$d_0 = R_{n,l=2}Y_{l=2,m=0}$$
$$d_1 = R_{n,l=2}Y_{l=2,m=1}$$
$$d_{-1} = R_{n,l=2}Y_{l=2,m=-1}$$
$$d_2 = R_{n,l=2}Y_{l=2,m=2}$$
$$d_{-2} = R_{n,l=2}Y_{l=2,m=-2}$$

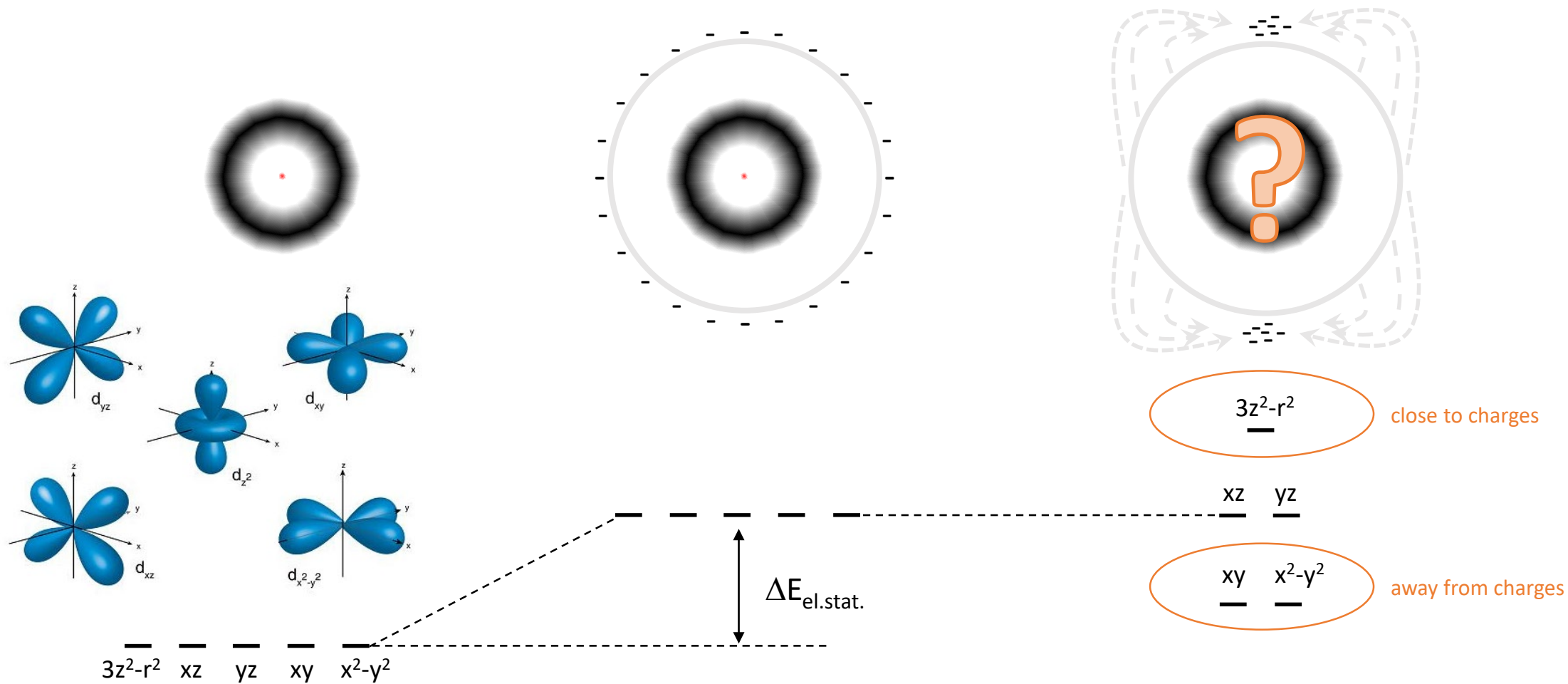
$$d_{3z^2-r^2} = d_0$$
$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(d_2 + d_{-2})$$
$$d_{xy} = \frac{-i}{\sqrt{2}}(d_2 - d_{-2})$$
$$d_{xz} = \frac{-1}{\sqrt{2}}(d_1 - d_{-1})$$
$$d_{yz} = \frac{i}{\sqrt{2}}(d_1 + d_{-1})$$

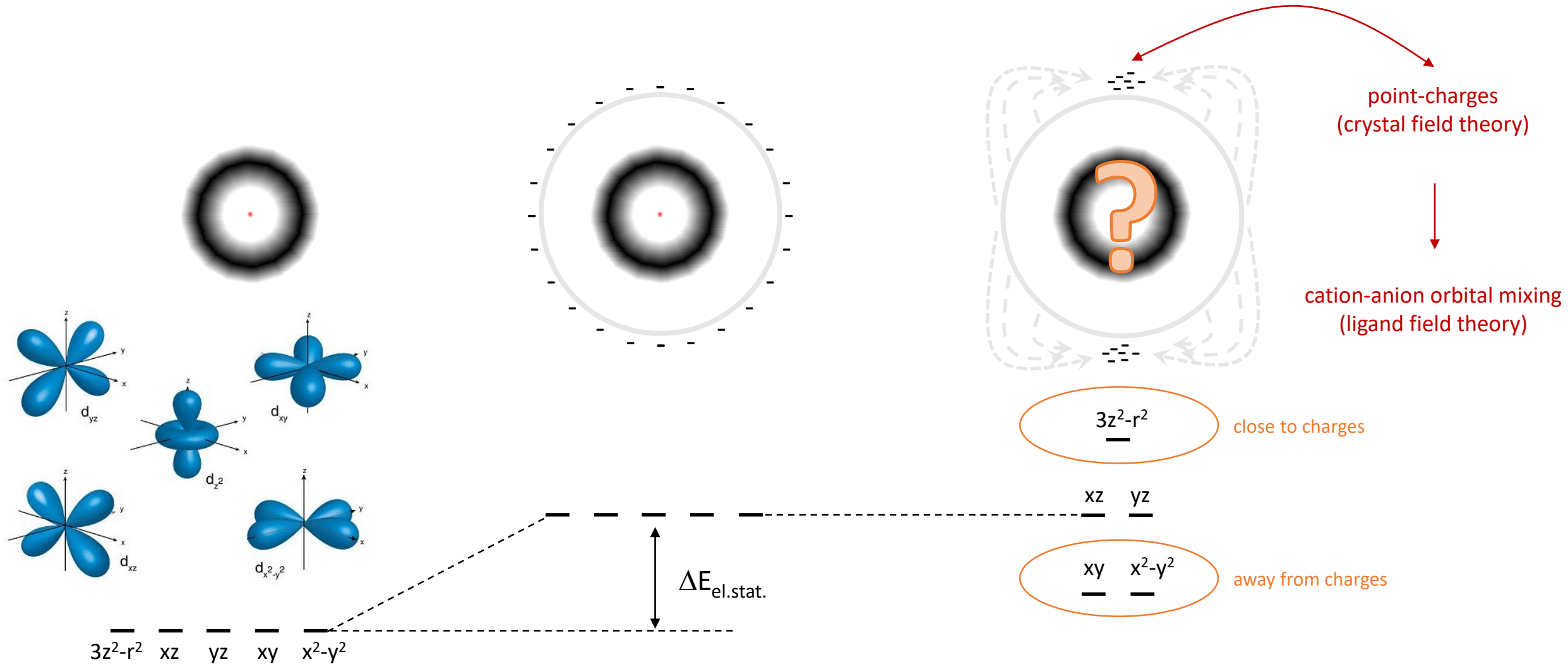


$$\overline{3z^2-r^2} \quad \overline{xz} \quad \overline{yz} \quad \overline{xy} \quad \overline{x^2-y^2}$$

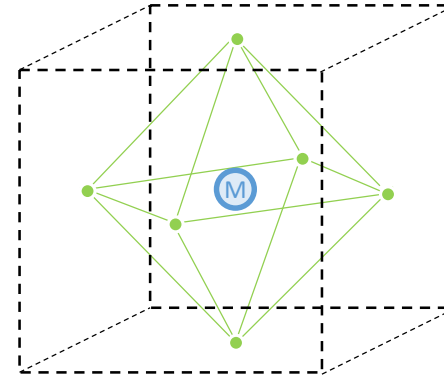




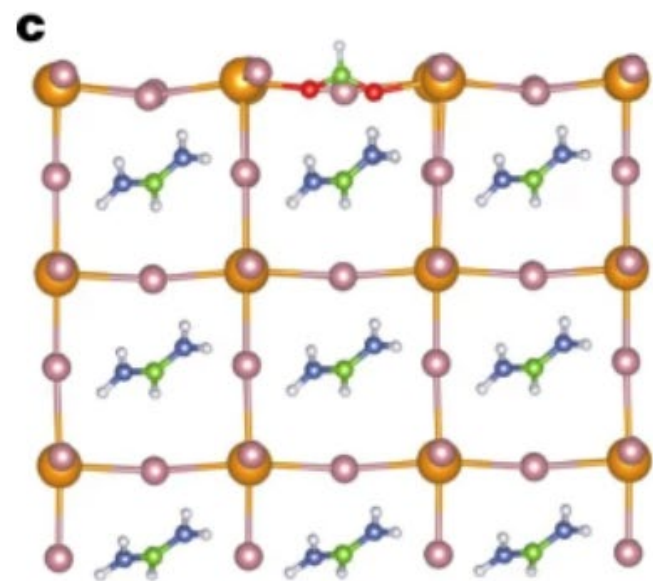
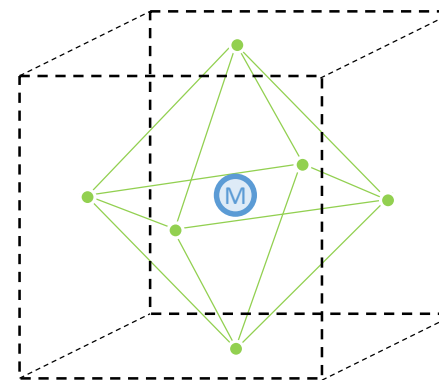




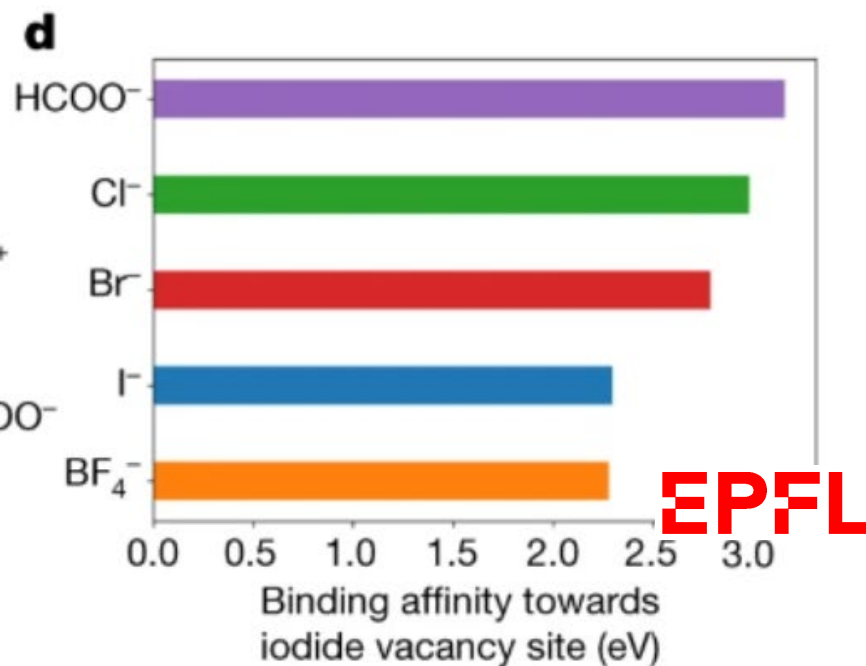
- ❖ 6 point charges
- ❖ equal distance from the magnetic ion (ideal case)



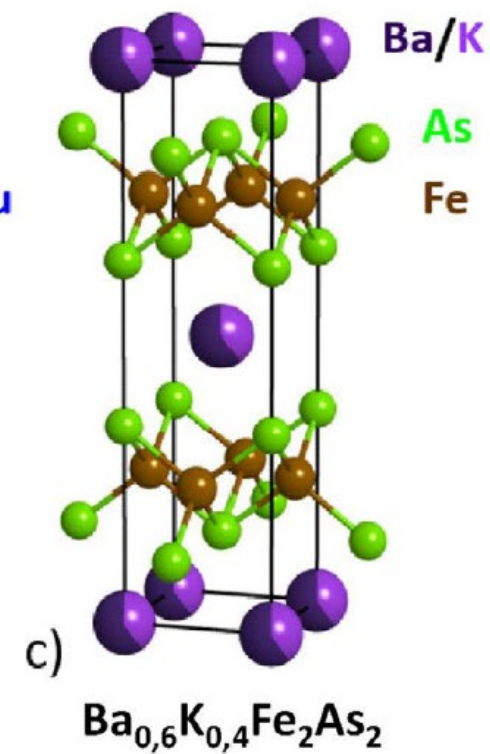
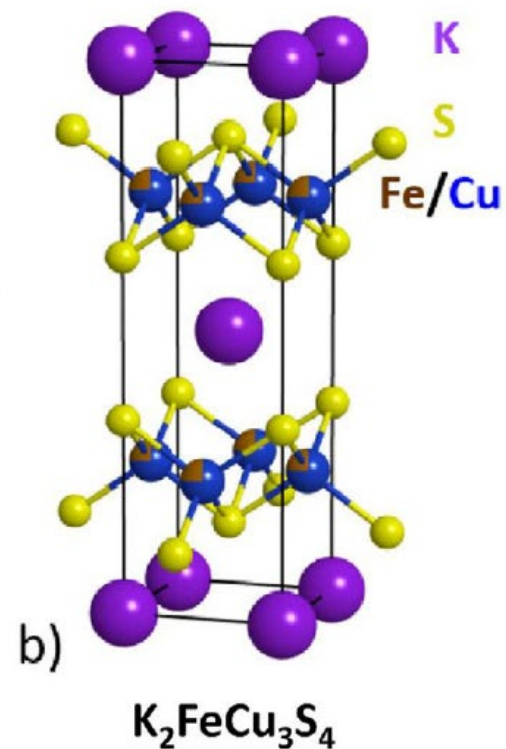
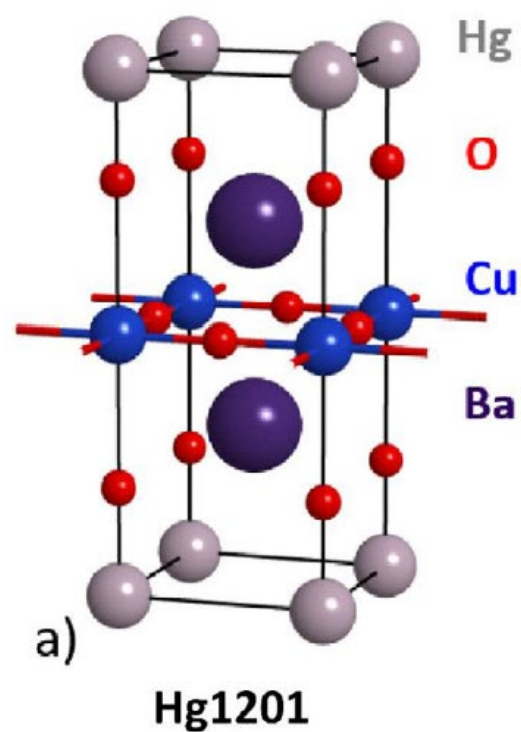
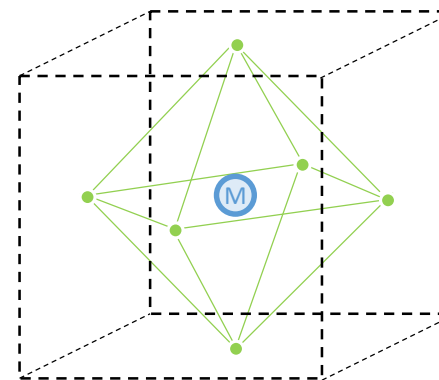
- ❖ 6 point charges
- ❖ equal distance from the magnetic ion (ideal case)
- ❖ ABO_3 (perovskites, new solar-cell materials)



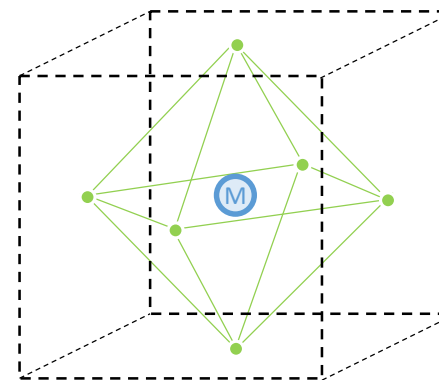
Nature 592, 381 (2021)



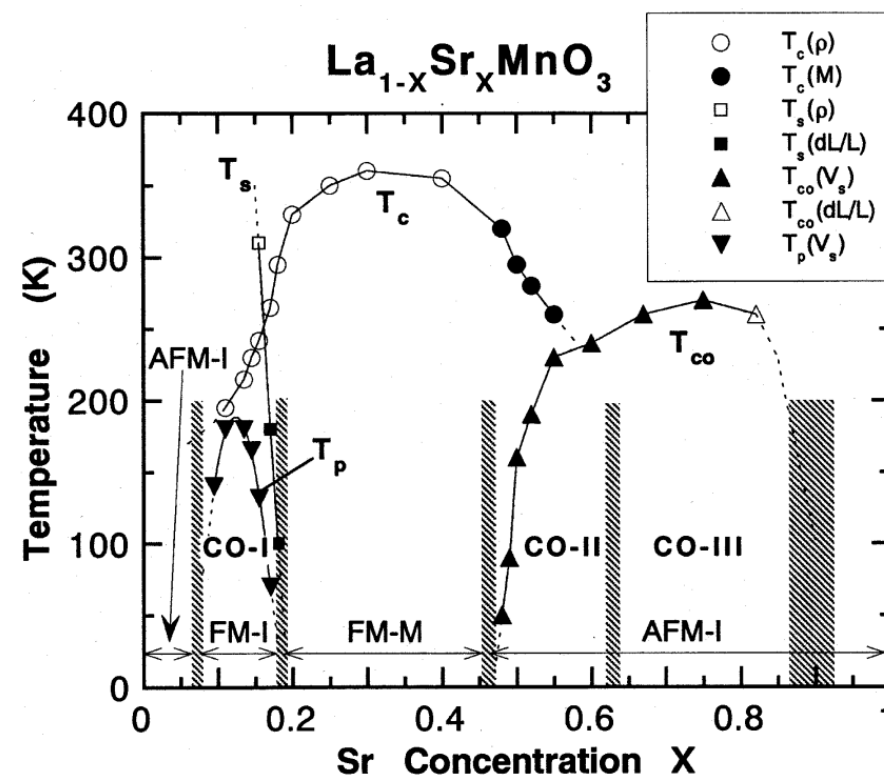
- ❖ 6 point charges
- ❖ equal distance from the magnetic ion (ideal case)
- ❖ ABO_3 (perovskites, new solar-cell materials)
- ❖ high- T_c superconductivity in cuprates



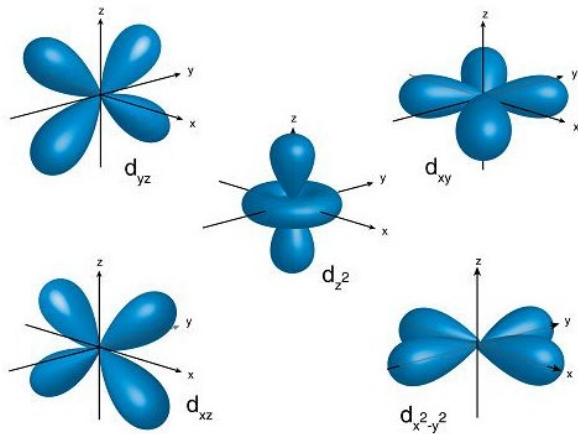
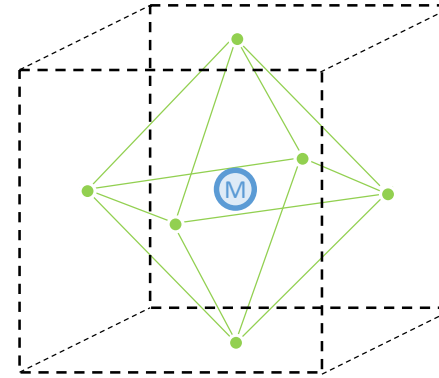
- ❖ 6 point charges
- ❖ equal distance from the magnetic ion (ideal case)
- ❖ ABO_3 (perovskites, new solar-cell materials)
- ❖ high- T_c superconductivity in cuprates
- ❖ colossal magnetoresistance in manganites



J. Phys. Soc. Jpn. 67, 2582 (1998)

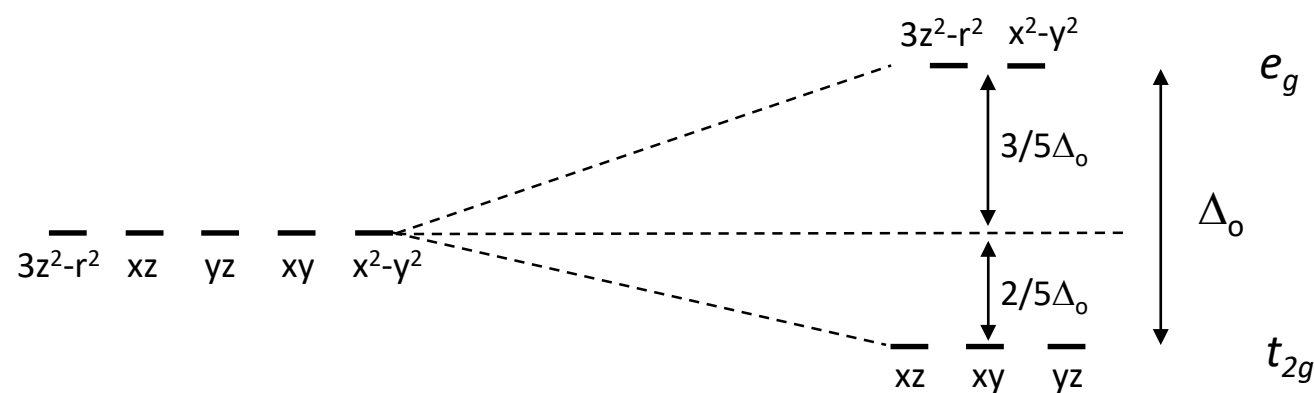
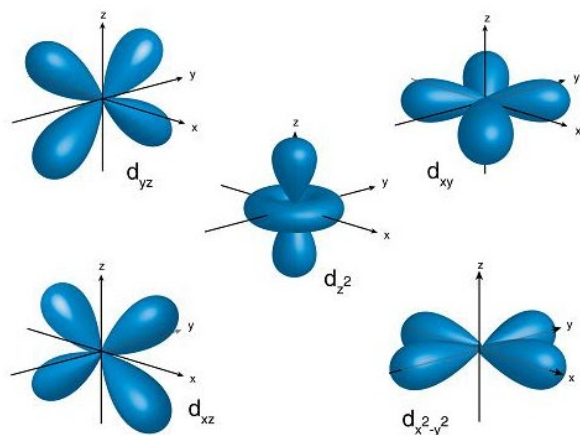
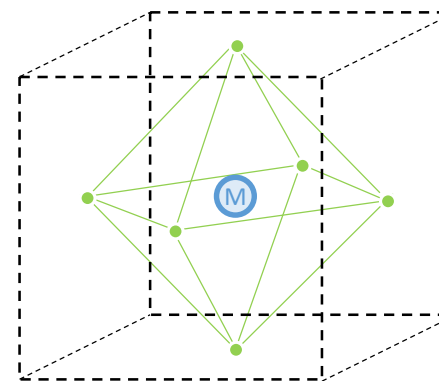


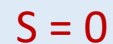
- ❖ 6 point charges
- ❖ equal distance from the magnetic ion (ideal case)
- ❖ ABO_3 (perovskites, new solar-cell materials)
- ❖ high-Tc superconductivity in cuprates
- ❖ colossal magnetoresistance in manganites



$$\overline{3z^2-r^2} \quad \overline{xz} \quad \overline{yz} \quad \overline{xy} \quad \overline{x^2-y^2}$$

- ❖ 6 point charges
- ❖ equal distance from the magnetic ion (ideal case)
- ❖ ABO_3 (perovskites, new solar-cell materials)
- ❖ high-Tc superconductivity in cuprates
- ❖ colossal magnetoresistance in manganites





1

H

Hydrogen

3

Li

Lithium

4

Be

Beryllium

11

Na

Sodium

12

Mg

Magnesium

19

K

Potassium

20

Ca

Calcium

37

Rb

Rubidium

55

Cs

Cesium

87

Fr

Francium

2

He

Helium

10

Ne

Neon

18

Ar

Argon

36

Kr

Krypton

54

Xe

Xenon

86

Rn

Radon

118

Uuo

Ununoctium

5

B

Boron

6

C

Carbon

7

N

Nitrogen

8

O

Oxygen

9

F

Fluorine

13

Al

Aluminium

14

Si

Silicon

15

P

Phosphorus

16

S

Sulfur

17

Cl

Chlorine

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

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

56

Ba

Barium

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

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

Uut

Ununtrium

114

Fl

Flerovium

115

Uup

Ununpentium

116

Lv

Livermorium

117

Uus

Ununseptium

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

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

Alkali

Alkaline

Transition

Lanthanoid

Actinoid

Post-transition

Metalloid

Nonmetal

Halogen

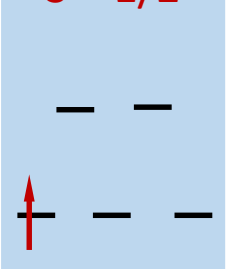
Noble gas

Unknown

d^1

$Sc^{2+}/Ti^{3+}/V^{4+}/Cr^{5+}$

$S = 1/2$



1 H Hydrogen																	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 Aluminium	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	*	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	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium				
		*	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				
		**	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				

d^2

Ti²⁺/V³⁺/Cr⁴⁺

$S = 1$

!!! maximize S !!!

1 H Hydrogen																	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 Aluminium	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	*	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	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium				
		*	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				
		**	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				

d^3

$V^{2+}/Cr^{3+}/Mn^{4+}$

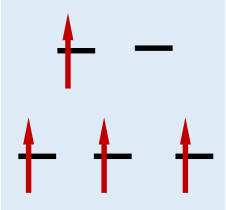
$S = 3/2$

1 H Hydrogen																	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 Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
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		**	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				

d^4

Cr^{2+}/Mn^{3+}

$S = 2$



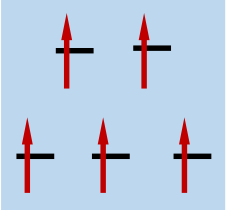
??? maximize S ???

1 H Hydrogen																	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 Aluminium	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	*	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	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium
		*	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
		**	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

d^5

Mn^{2+}/Fe^{3+}

$S = 5/2$



1 H Hydrogen																	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 Aluminium	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	*	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	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium
		*	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
		**	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

d^6

$\text{Fe}^{2+}/\text{Co}^{3+}$

$S = 2$

1 H Hydrogen																	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 Aluminium	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	*	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	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium				
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d^7

Co^{2+}

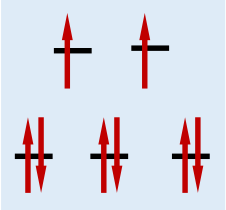
$S = 3/2$

1 H Hydrogen																	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 Aluminium	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	*	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	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium
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d^8

Ni²⁺

$S = 1$

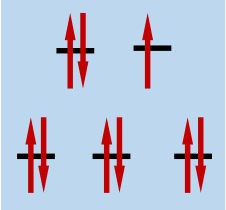


1 H Hydrogen																	2 He Helium				
3 Li Lithium	4 Be Beryllium															5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium															13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 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				
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87 Fr Francium	88 Ra Radium	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium				
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d^9

Cu^{2+}

$S = 1/2$

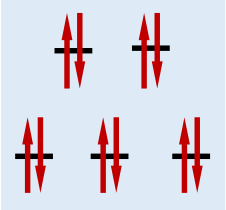


1 H Hydrogen																	2 He Helium				
3 Li Lithium	4 Be Beryllium															5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium															13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 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				
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d^{10}

Cu¹⁺/Zn²⁺

$S = 0$



1 H Hydrogen																	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 Aluminium	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	*	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	**	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium				
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Alkali

Alkaline

Transition

Lanthanoid

Actinoid

Post-transition

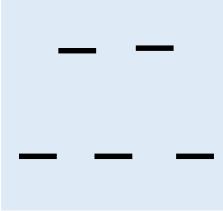
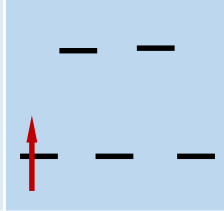
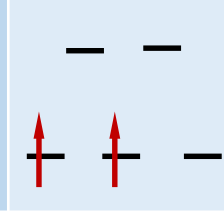
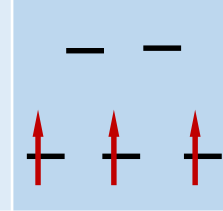
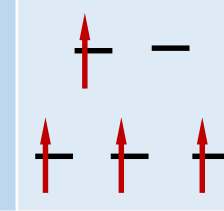
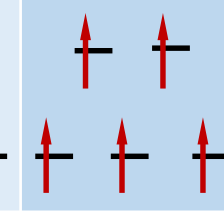
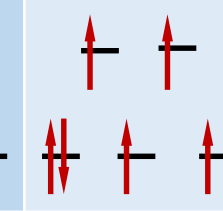
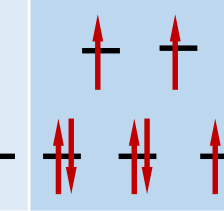
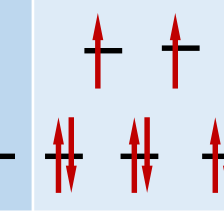
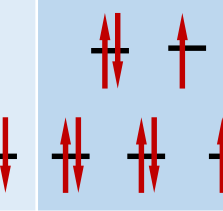
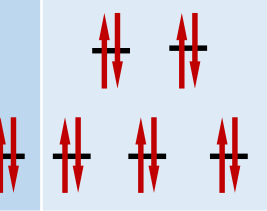
Metalloid

Nonmetal

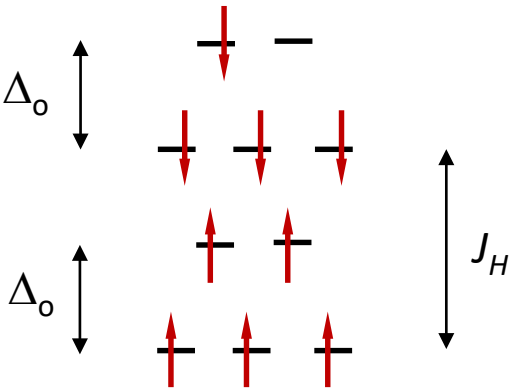
Halogen

Noble gas

Unknown

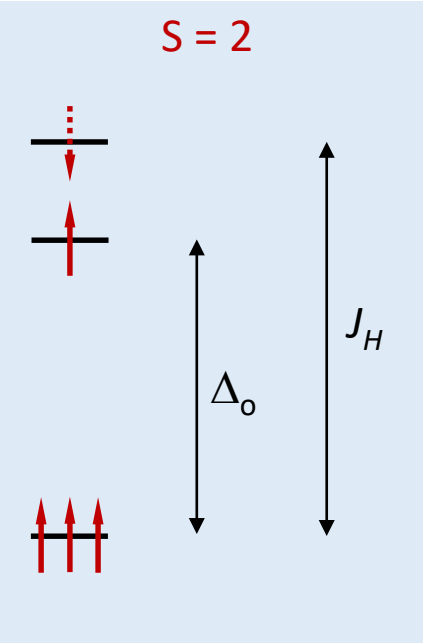
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$
										

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$



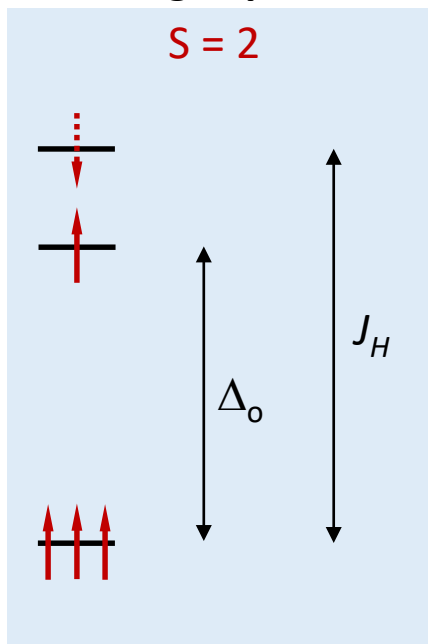
-> see Matthiesen *PRL* **130**, 076702 (2023)

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$



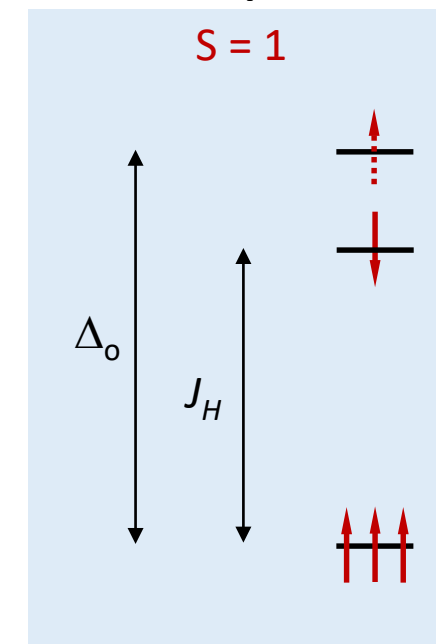
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$

high spin

 $S = 2$ 

- ❖ if there would be no electron-electron repulsion ($J_H = 0$) $\rightarrow S = 1$
- ❖ if $J_H > 0$ but $J_H < \Delta_o \rightarrow S = 1$
- ❖ if $J_H > \Delta_o \rightarrow S = 2$

low spin

 $S = 1$ 

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$

high spin

$S = 2$

low spin

$S = 1$

$S = 1$

$S = 1/2$

$S = 0$

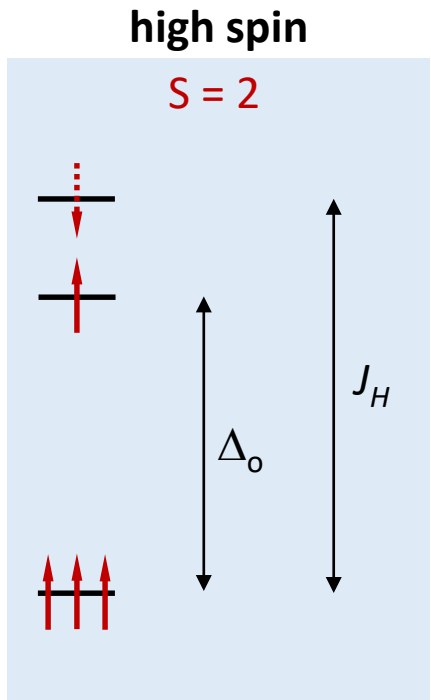
$S = 1/2$

❖ if there would be no electron-electron repulsion ($J_H = 0$) $\rightarrow S = 1$

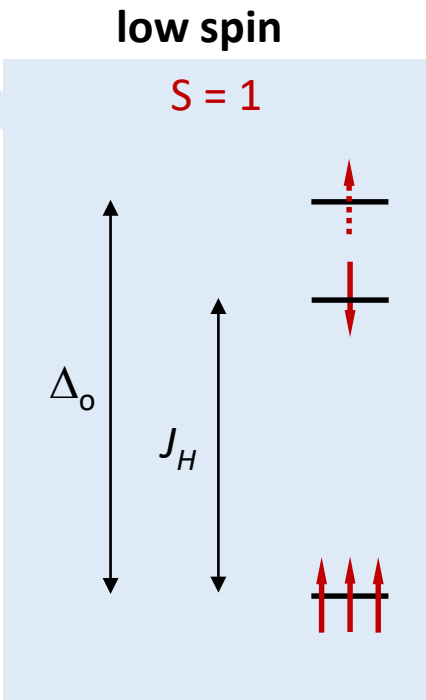
❖ if $J_H > 0$ but $J_H < \Delta_o \rightarrow S = 1$

❖ if $J_H > \Delta_o \rightarrow S = 2$

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$



$S = 1$	$S = 1/2$	$S = 0$	$S = 1/2$

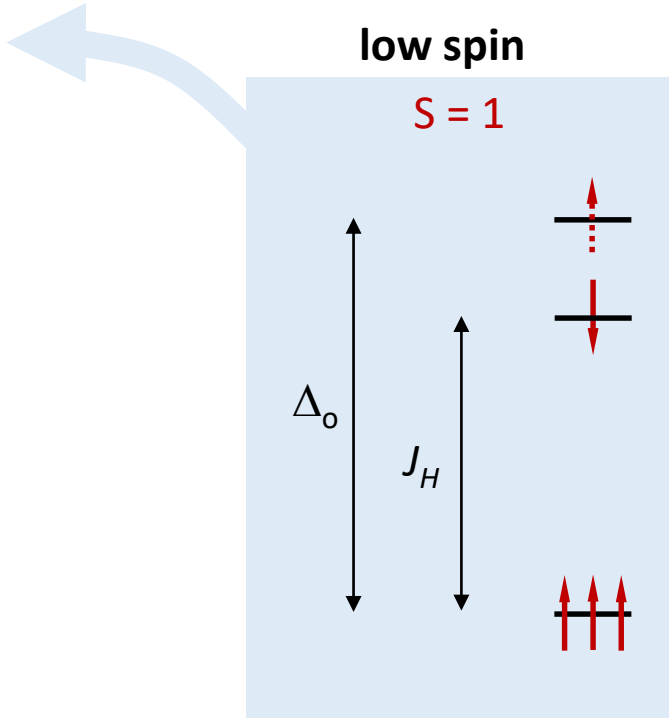
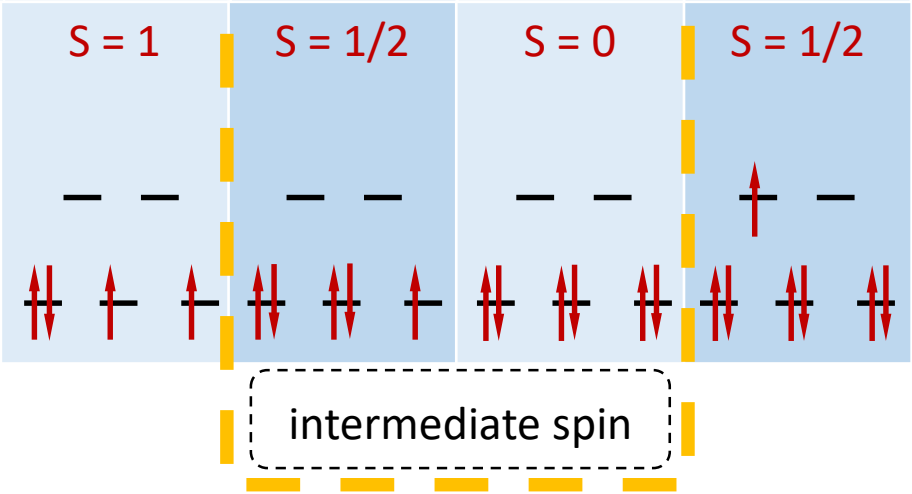
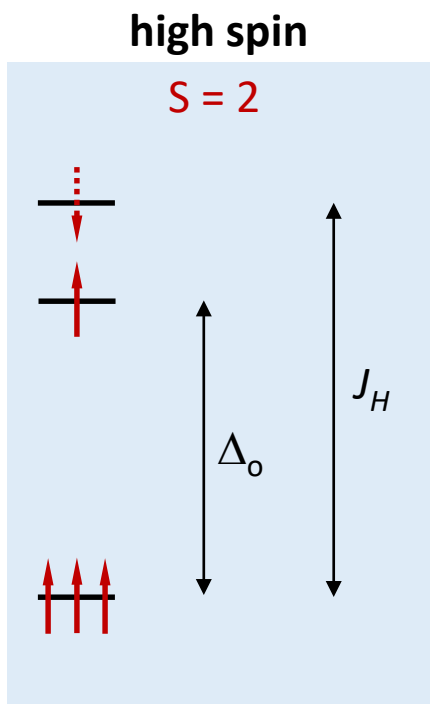


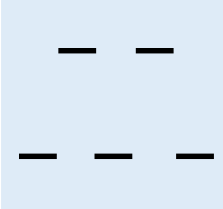
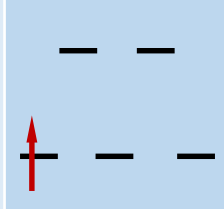
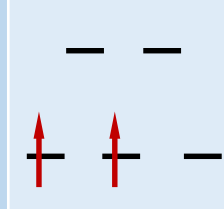
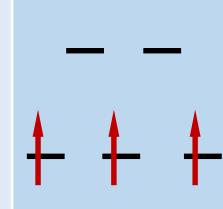
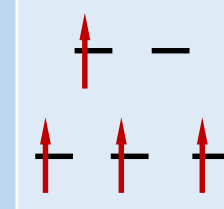
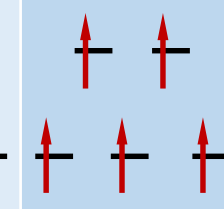
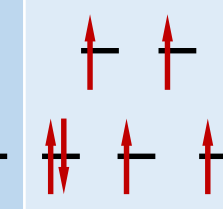
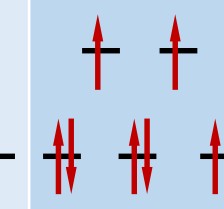
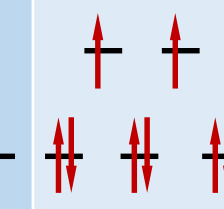
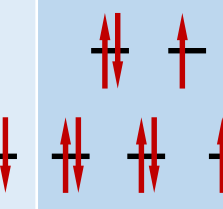
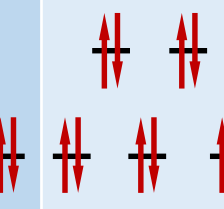
ABSTRACT

Phys. Rev. Lett. **97**, 146405

The *ab initio* self-interaction-corrected local-spin-density approximation is used to study the electronic structure of both stoichiometric and nonstoichiometric nickelates. From total energy considerations it emerges that, in their ground state, both LiNiO₂ and NaNiO₂ are insulators, with the Ni ion in the Ni³⁺ low-spin state (*t*_{2g}⁶*e*_g¹) configuration. It is established that a substitution

d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$

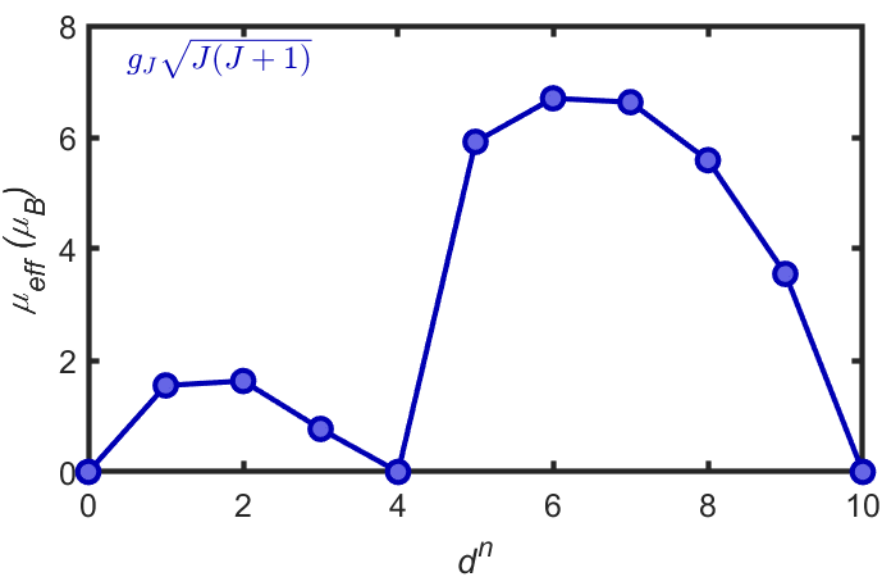


d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$
										
L = 0	L = 2	L = 3	L = 3	L = 2	L = 0	L = 2	L = 3	L = 3	L = 2	L = 0

↑

$\Sigma = 2 + 1 + 0 + (-1) = 2$

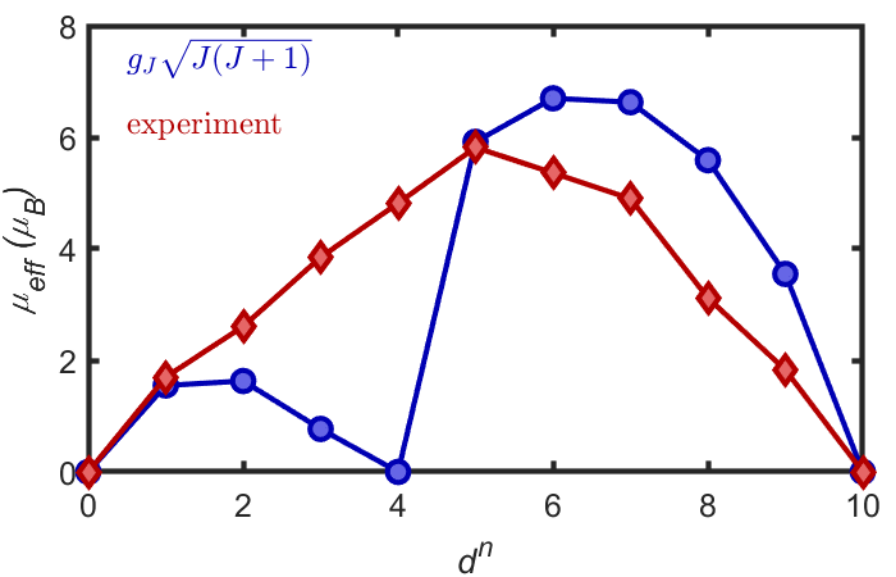
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$
$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$



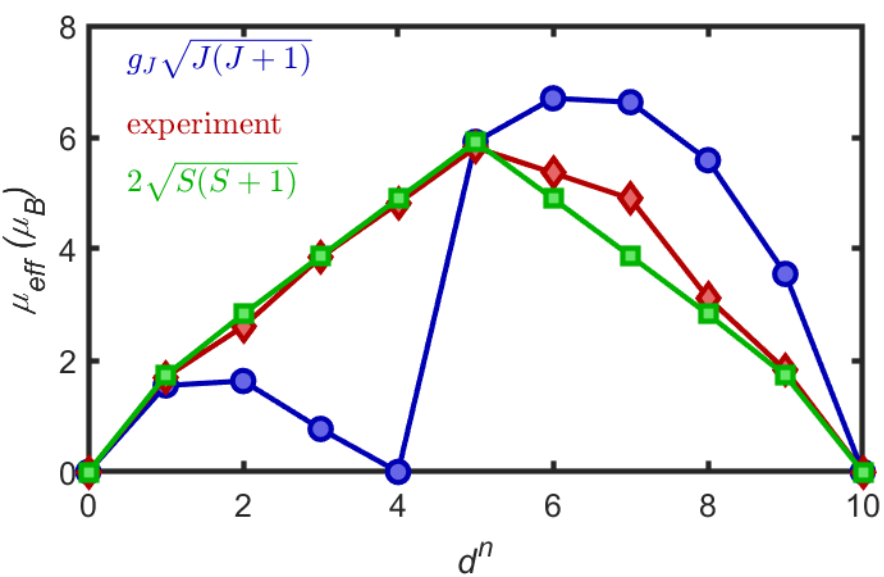
$$\chi = \frac{N_A \mu_0 g_J^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{C}{T} = \frac{N_A \mu_0 \mu_{eff}^2}{3k_B T}$$

$$\mu_{eff}^2 = g_J^2 \mu_B^2 J(J+1)$$

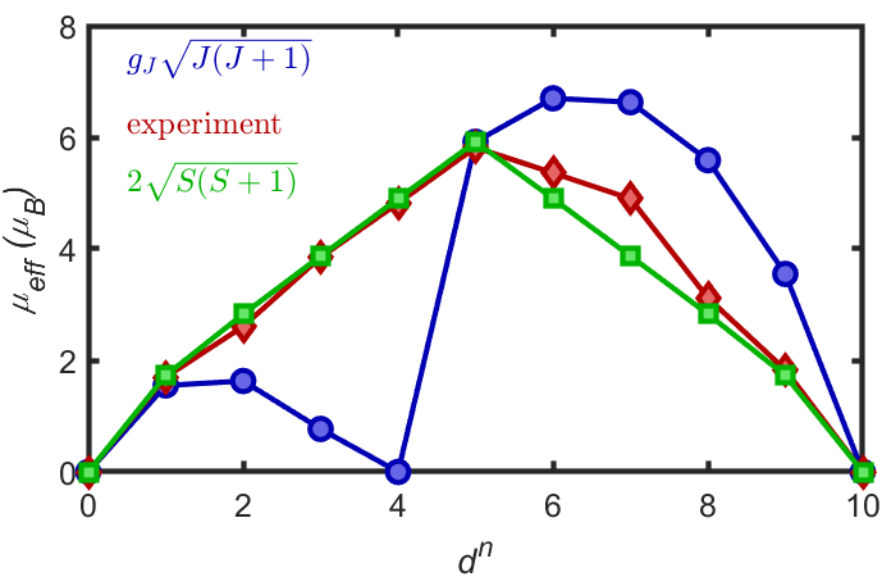
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$
$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$



d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$
$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$



d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$
$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$



❖ $\mathbf{J} = \mathbf{L} + \mathbf{S}$ does not work

$\mathcal{H}_0 > \mathcal{H}_{CF} > \mathcal{H}_{SO} \gg \mathcal{H}_Z$

❖ L is ‘quenched’

❖ point charges break the rotational symmetry

$$V_{CF}^{oct}(r) \sim x^4 + y^4 + z^4 - \frac{3}{5}r^4$$

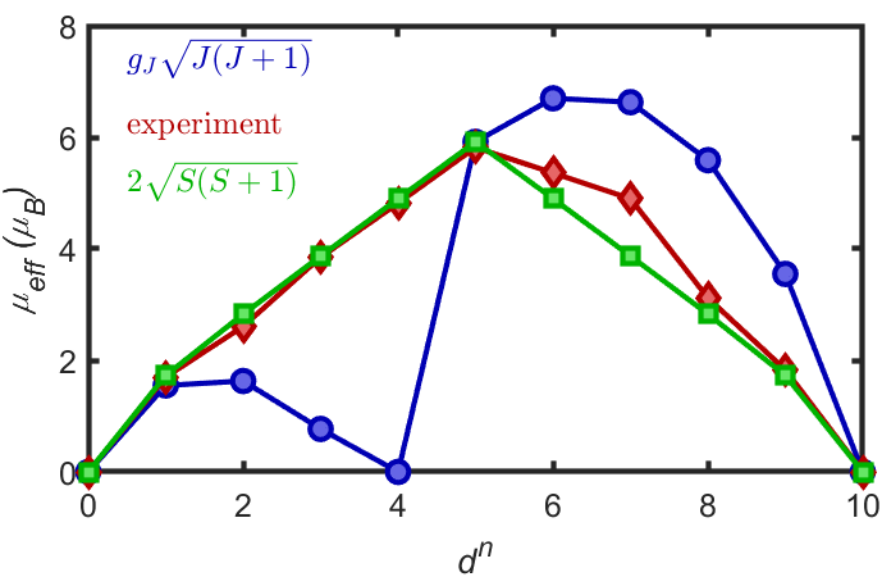
$$\hat{\mathbf{L}} = -i\hat{\mathbf{r}} \times \nabla$$

real

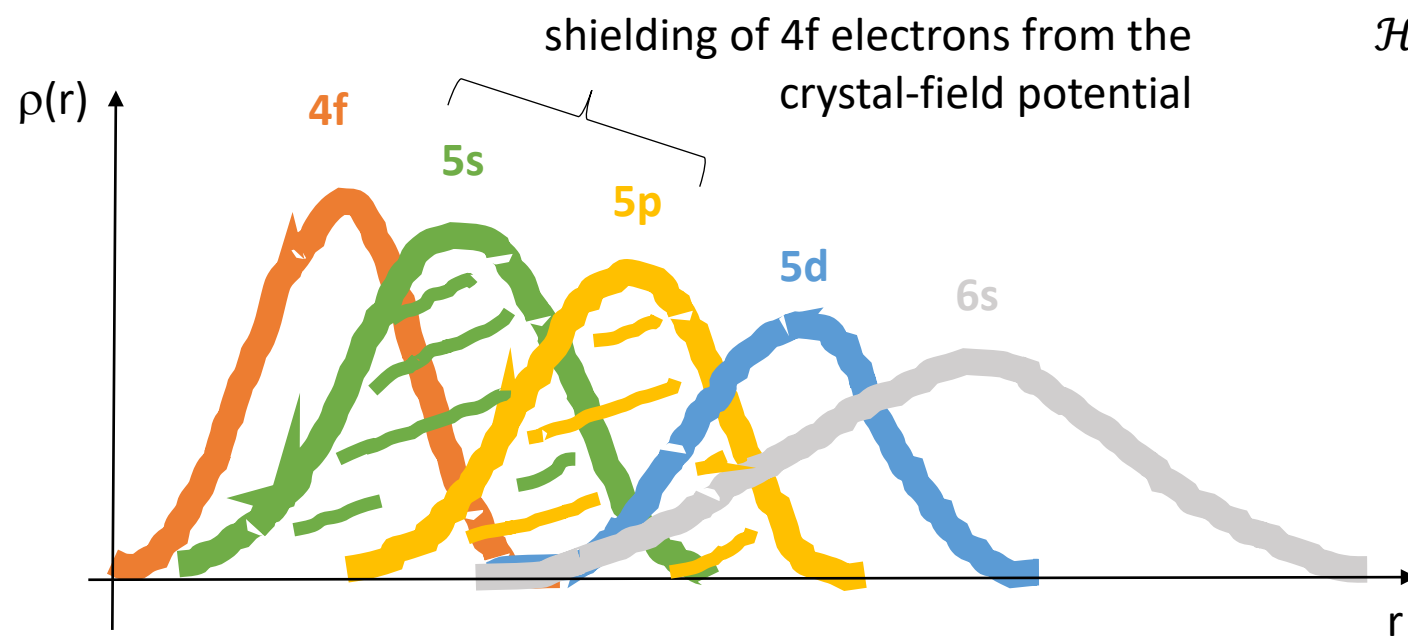
imaginary

Hermitian, so $\langle 0|\hat{\mathbf{L}}|0\rangle \in \mathbb{R}$ only if $\langle 0|\hat{\mathbf{L}}|0\rangle = 0$

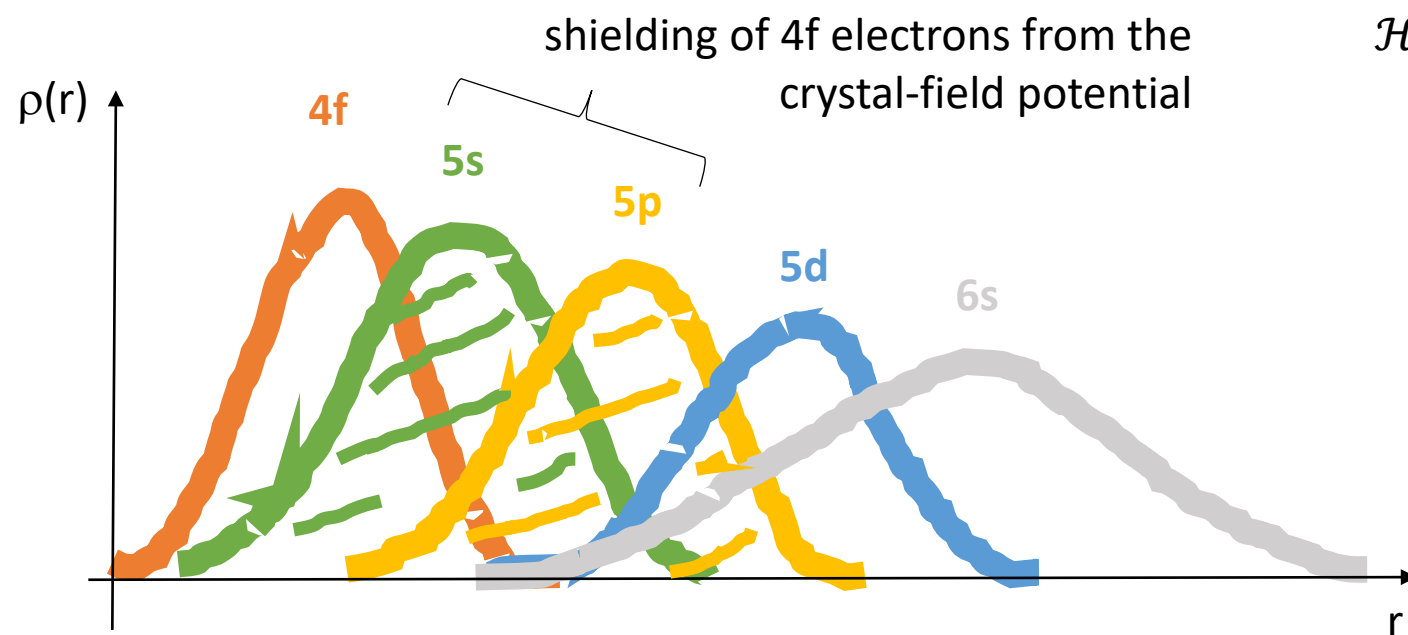
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc ³⁺ /Ti ⁴⁺ /V ⁵⁺	Sc ²⁺ /Ti ³⁺ /V ⁴⁺ /Cr ⁵⁺	Ti ²⁺ /V ³⁺ /Cr ⁴⁺	V ²⁺ /Cr ³⁺ /Mn ⁴⁺	Cr ²⁺ /Mn ³⁺	Mn ²⁺ /Fe ³⁺	Fe ²⁺ /Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cu ¹⁺ /Zn ²⁺
$S = 0$	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = 2$	$S = 3/2$	$S = 1$	$S = 1/2$	$S = 0$
$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$	$L = 2$	$L = 3$	$L = 3$	$L = 2$	$L = 0$



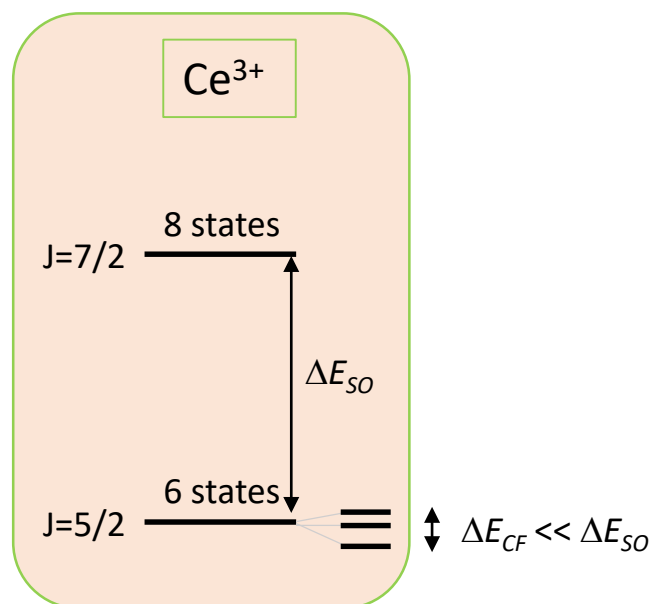
- ❖ in practice: incomplete quenching
 - t_{2g} subset ($n=1,2,6,7$), ‘effective’ $L = 1$
 - spin-orbit coupling
- ❖ reflected in $g > 2$ and often anisotropic

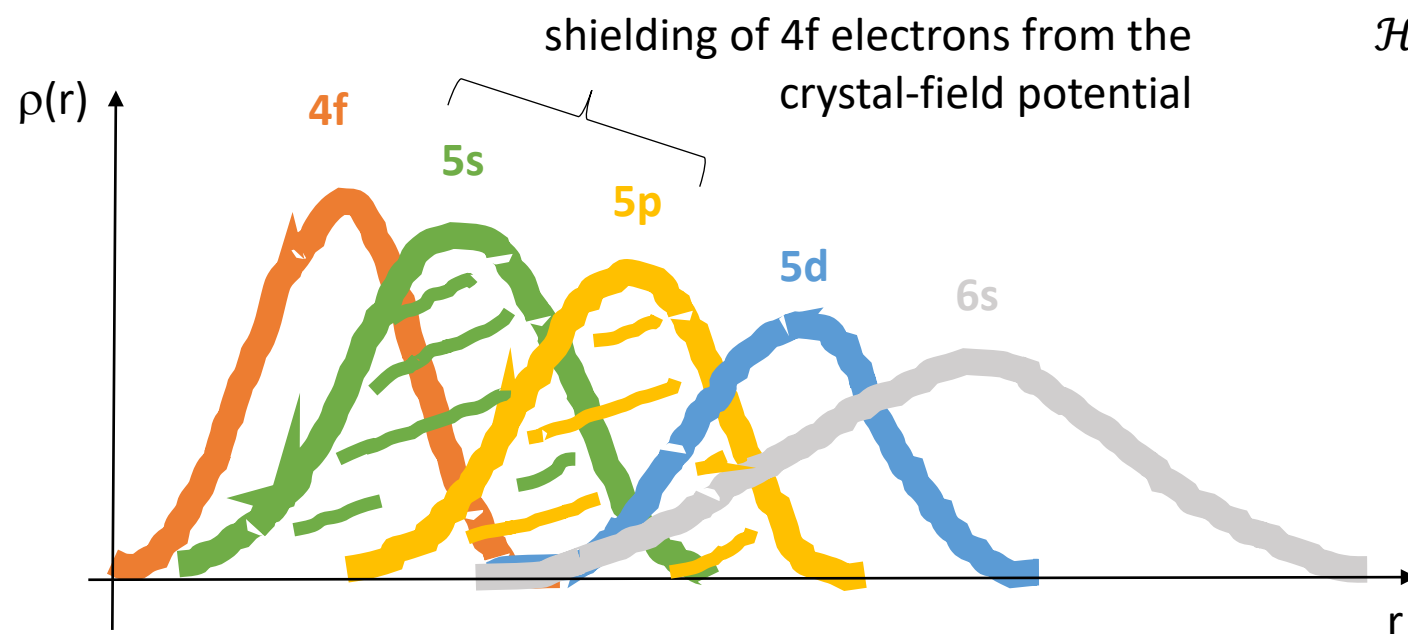


$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$

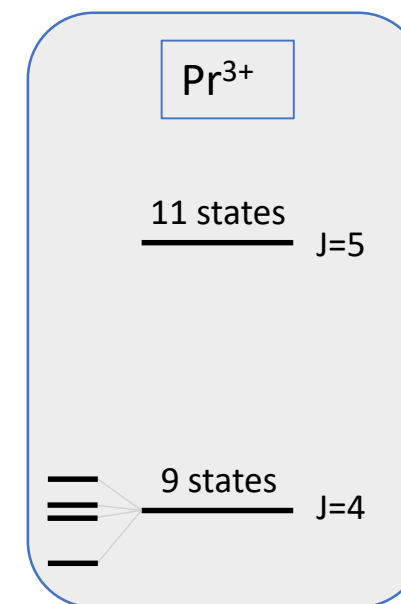
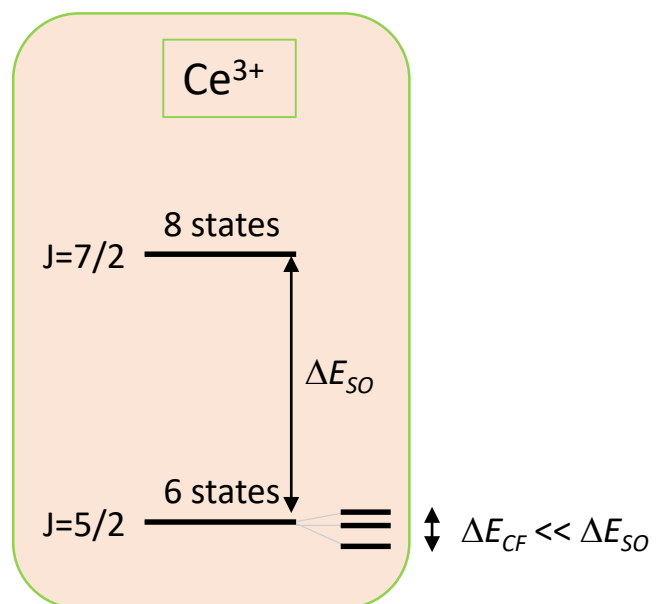


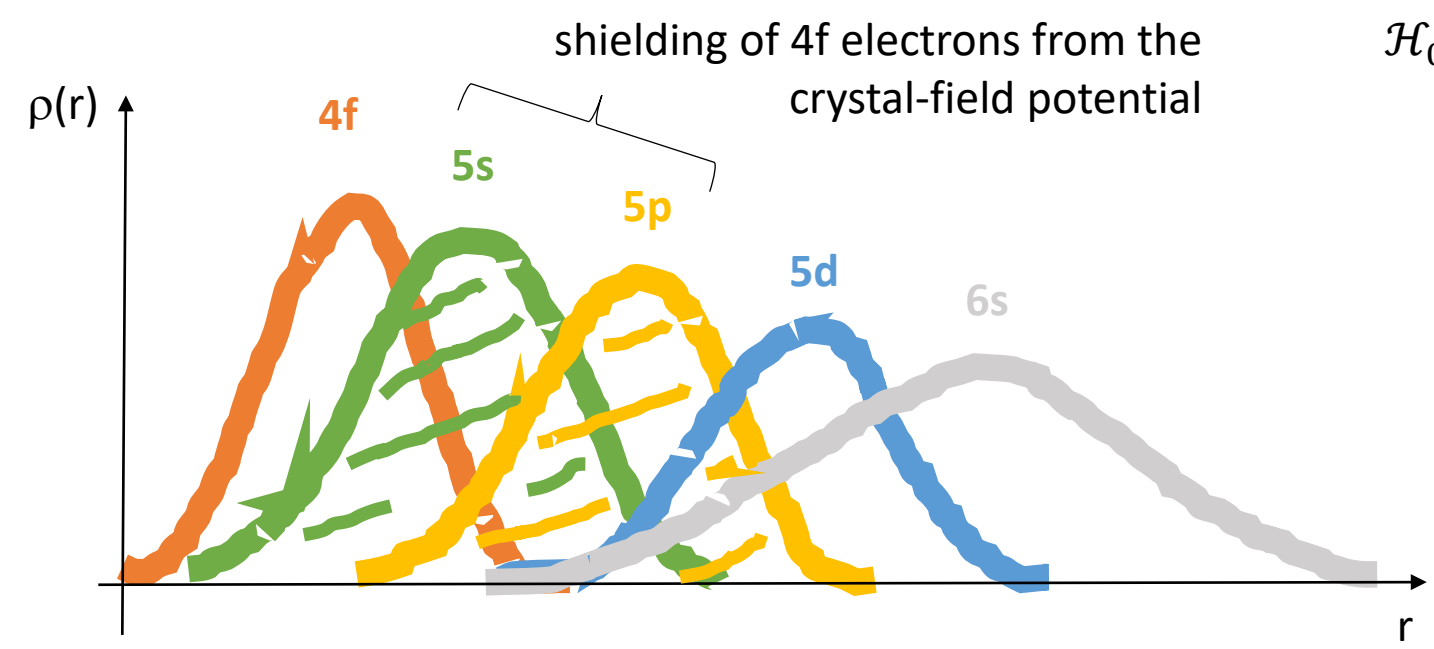
$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$



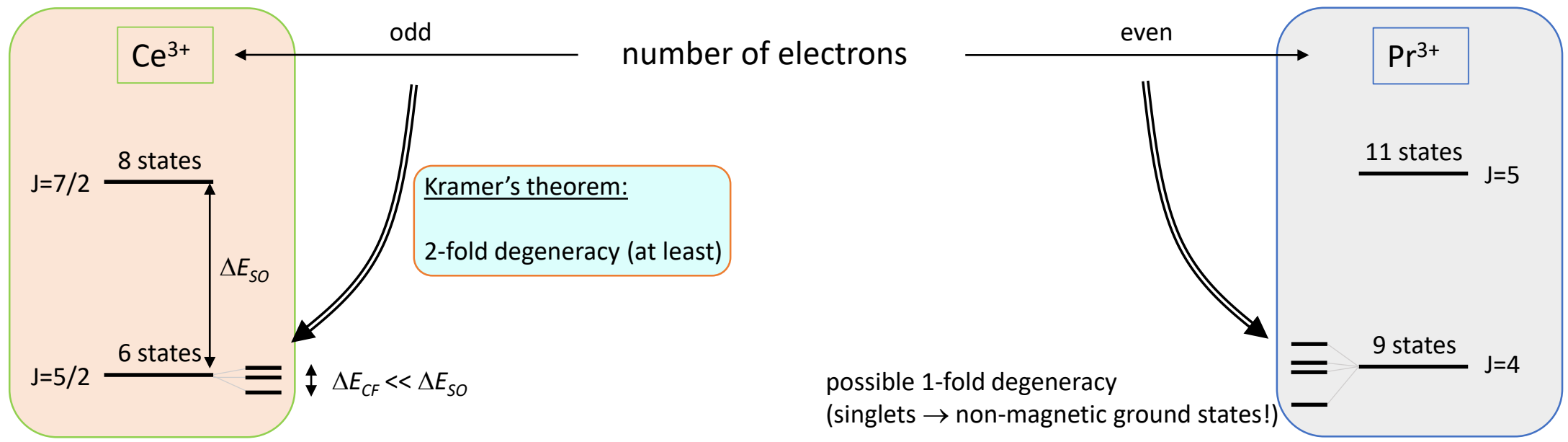


$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$





$$\mathcal{H}_0 > \mathcal{H}_{SO} > \mathcal{H}_{CF} > \mathcal{H}_Z$$



octahedral

$$\begin{array}{cc} \overline{3z^2-r^2} & \overline{x^2-y^2} \\ \\ \overline{xz} & \overline{xy} & \overline{yz} \end{array}$$

tetragonal compression

$$\begin{array}{cc} \overline{3z^2-r^2} \\ \overline{x^2-y^2} \\ \\ \overline{xz} & \overline{yz} \\ \overline{xy} \end{array}$$

tetragonal elongation

$$\begin{array}{cc} \overline{x^2-y^2} \\ \overline{3z^2-r^2} \\ \\ \overline{xy} \\ \overline{xz} & \overline{yz} \end{array}$$

square planar

$$\begin{array}{cc} \overline{x^2-y^2} \\ \\ \overline{xy} \\ \overline{3z^2-r^2} \\ \overline{xz} & \overline{yz} \end{array}$$

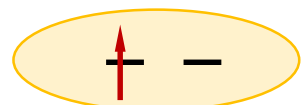
trigonal prism

$$\begin{array}{cc} \overline{xz} & \overline{yz} \\ \\ \overline{3z^2-r^2} & \overline{xy} & \overline{x^2-y^2} \end{array}$$

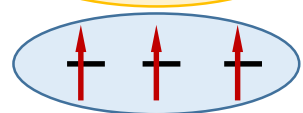
tetrahedral

$$\begin{array}{ccc} \overline{xz} & \overline{xy} & \overline{yz} \\ \\ \overline{3z^2-r^2} & \overline{x^2-y^2} \end{array}$$

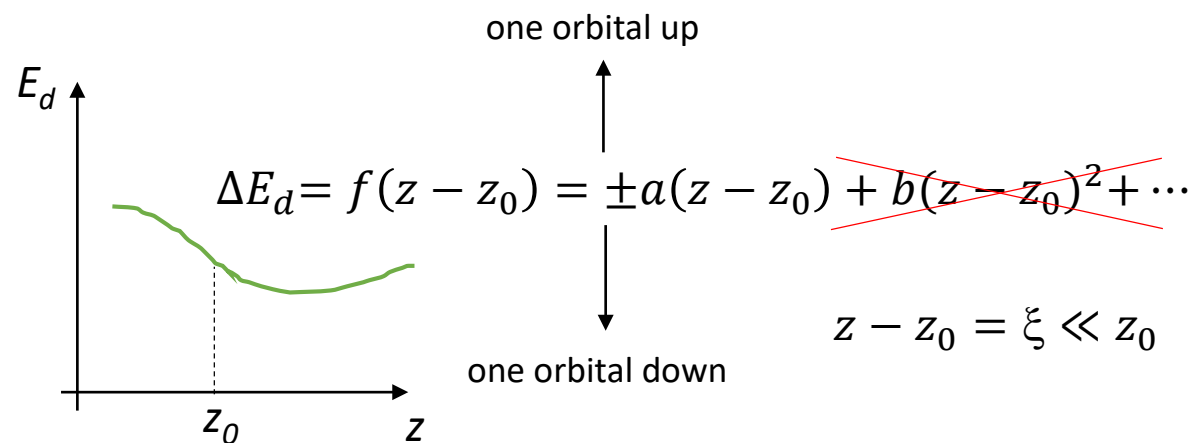
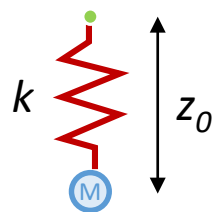


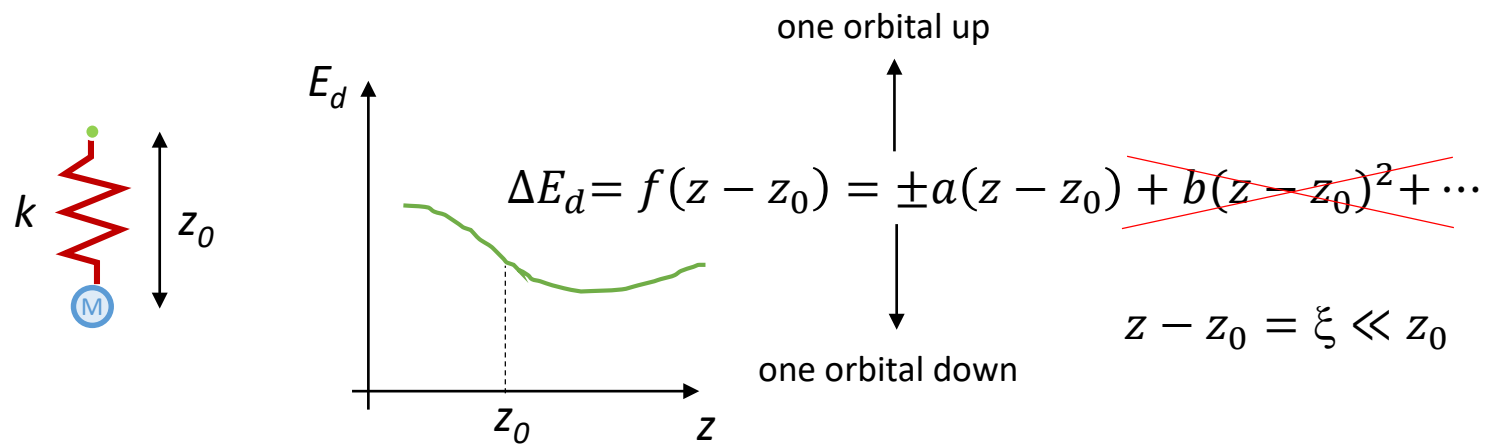


doubly degenerate



no degeneracy



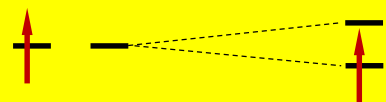


$$E_{elas} = \frac{1}{2}k(z - z_0)^2$$

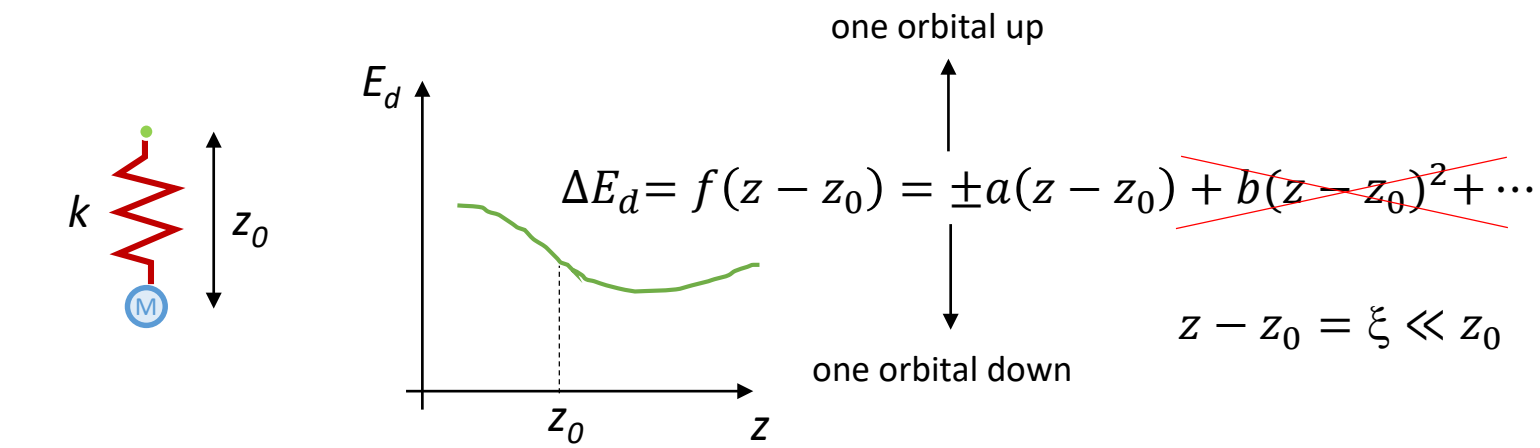
$$E_{tot} = \pm a\xi + \frac{1}{2}k\xi^2$$

$$\frac{dE_{tot}}{d\xi} = \pm a + k\xi = 0$$

$\xi_{JT} = \pm \frac{a}{k}$



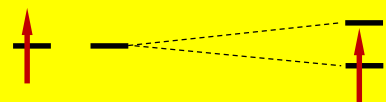
static JT



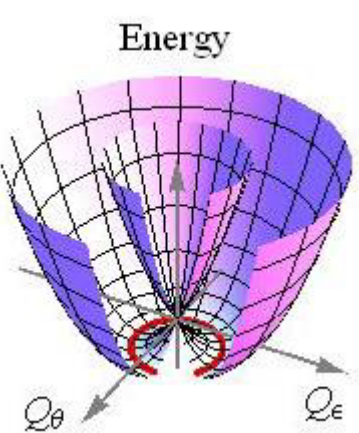
$$E_{elas} = \frac{1}{2}k(z - z_0)^2$$

$$E_{tot} = \pm a\xi + \frac{1}{2}k\xi^2$$

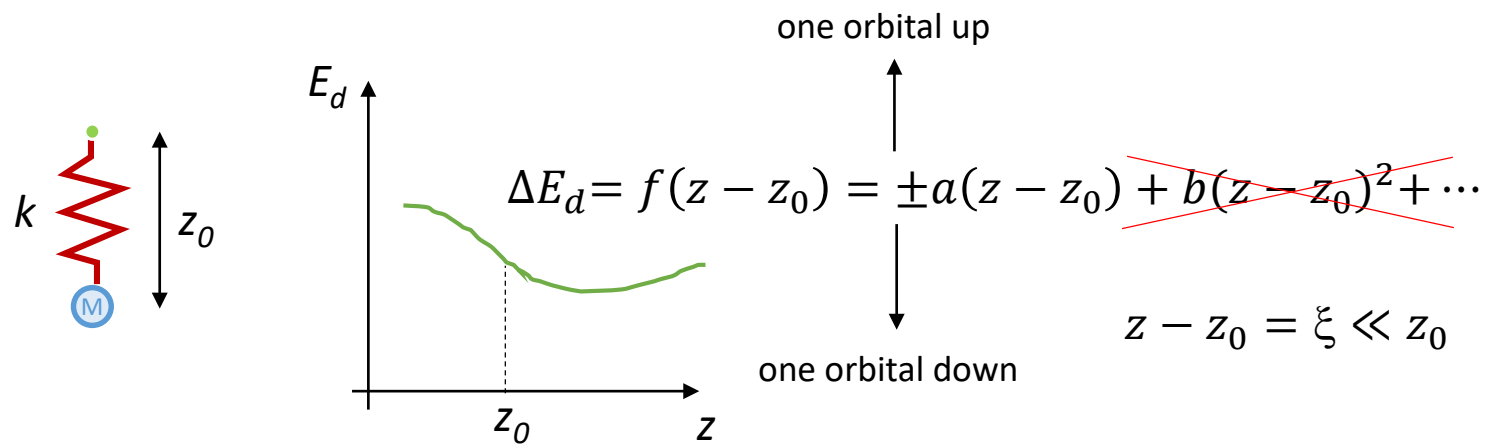
$$\frac{dE_{tot}}{d\xi} = \pm a + k\xi = 0$$

$\xi_{JT} = \pm \frac{a}{k}$


static JT

$$\xi \rightarrow \sqrt{Q_\theta^2 + Q_\epsilon^2}$$


dynamic JT



$$E_{elas} = \frac{1}{2}k(z - z_0)^2$$

$$E_{tot} = \pm a\xi + \frac{1}{2}k\xi^2$$

$$\frac{dE_{tot}}{d\xi} = \pm a + k\xi = 0$$

