

Crystal field and spin Hamiltonian
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Abstract

In studying the magnetic properties of any ionic solid, it is important to know what kind of magnetic ions are present and how they are situated in the lattice. The magnetic properties of a given ion are usually profoundly influenced by the electric fields of neighboring ions. In general, the energy level diagram of the ion consists of a low-lying group, with an overall spacing of probably less than typically 1 cm^{-1} , and a large gap to the next set of levels. From general perturbation theory considerations, considerable mixing of the low-lying states must be expected, but admixture of the higher excited states are likely to be small and can be neglected. Then it is a good approximation to assume that the ion only has the low-lying states. This is the spin Hamiltonian approximation- to replace the Hamiltonian of the ion, with all its states, by another Hamiltonian which accurately describes only the low-lying states. It is valuable to recognize that the spin Hamiltonian does two distinct things. It first provides a means of setting down in a compact way, the results of many measurements, all of which can be retrieved by suitable manipulations. It also provides a starting (or end) point for a detailed theoretical discussion of the ion in its environment.

In this note, a spin Hamiltonian, which first appears in the work of Van Vleck,¹ is introduced. A mass of experimental information can be summed up succinctly in a spin Hamiltonian in just the way that the theoretician finds most acceptable, and the experimentalists reasonably comprehensible. If there are n states, the matrix representation of the spin Hamiltonian, using any axis of quantization, will be a finite Hermitian ($n \times n$) matrix. Its matrix elements will depend on the magnitude and direction of the magnetic field and on the axis of quantization.

In this note, we use the Mathematica to obtain the calculations of expansion of the crystal field, $2p$ and $3d$ wavefunctions, the matrix elements over the wavefunctions, eigenvalue problems based on the quantum mechanics. These procedures make it much easier for students (who are not familiar with quantum mechanics) to understand the essential point of magnetism. We show how to derive the eigenvalue problems for the spin Hamiltonian of the magnetic ions in the crystal field. It is sometime complicated for the system having many electrons. We note that there are many excellent textbooks on the magnetism, including White² (Quantum Theory of Magnetism), Kittel³ (Introduction to Solid State Physics), and Yosida⁴ (Theory of Magnetism). Students in Japan study magnetism using famous textbook of Kanamori⁵ (Magnetism), and Date⁶ (Electron Spin Resonance). These books are written in Japanese.

One of the authors (MS) has been studying the magnetic properties of quasi two-dimensional magnetic systems such as Rb_2CoF_4 , stage-2 CoCl_2 -, NiCl_2 -, CrCl_3 -, MnCl_2 -, FeCl_3 -, and CuCl_2 - graphite intercalation compounds (GIC's) using SQUID magnetometer and magnetic neutron scattering since 1977. This note is written from a view point of experimentalist, rather than theorists.

Contents

1. Introduction: a brief history on the modern magnetism

2. Fundamentals
 - 2.1. Angular momentum and Magnetic momentum of one electron
 - 2.2. Periodic table of iron group elements
 - 2.3. Magnetic moment of atom
 - 2.4. Spin-orbit interaction in an electron around the nucleus
3. Hund's rule
 - 3.1. Electron states in the atom
 - 3.2. The electron configuration $(3d)^n$ ($n = 1 - 10$)
 - 3.3. Spin orbit interaction of isolated atom
4. Crystal field
 - 4.1. Overview
 - 4.2. Series expansion of the crystal field
 - 4.3. Mathematica program
 - 4.4. Summary
5. p -electrons: quenching of the orbital angular momentum;
 - 5.1. $2p$ -electron wave functions
 - 5.2. $2p$ electron in the octahedral field
 - 5.3. Quenching of orbital angular momentum
 - A. Orbital angular momentum (quantum mechanics)
 - B. Calculation of orbital angular momentum by Mathematica
 - C. Theorem
 - 5.4. Zeeman splitting of the orbital energy levels
 - 5.5. Mathematica program: eigenvalue problem
6. $3d$ -electrons in the crystal field
 - 6.1. $3d$ -electron wave functions
 - 6.2. Orthorhombic crystal field
 - 6.3. Wave function of $(3d)^1$ electron in the orthorhombic field
 - 6.4. Wave function of $(3d)^1$ electron in the tetragonal field
 - A. Eigenvalue problem
 - B. Eigenvalue problem
 - C. Mathematica program: Eigenvalue problem
 - D. Quenching of orbital angular momentum
 - E. Mathematica program
7. The energy diagram of Cu^{2+} with $(3d)^9$ electron configuration: Rule-1
8. Energy diagram of $(3d)^n$ electron configuration
 - 8.1. Rule-2
 - 8.2. Ground state for $(3d)^n$ electron configuration ($n > 1$)
 - 8.3. Excited states for $(3d)^2$ electron configuration
 - 8.4. Excited states for $(3d)^3$ electron configuration
 - 8.5. Excited states of $(3d)^1$ electron configuration
 - 8.6. Excited states of $(3d)^4$ electron configuration
 - 8.7. Energy diagram: application of rule-1 and rule-2
9. Jahn-Teller effect
10. Low spin and high spin states
11. Spin Hamiltonian of spin systems with the orbital singlet as a ground state
 - 11.1. Pryce spin Hamiltonian

- 11.2 g-factors and the single ion anisotropy D
 - A. Definition
 - B. g-factors in Cu^{2+} ion in the tetragonal field ($c > a = b$)
 - 11.3 Ni^{2+}
 - 11.4 Cr^{3+}
 - 12. Spin Hamiltonian for $S = 1/2, 1, 3/2, 2$ and $5/2$
 - 12.1 $S = 1/2$
 - 12.2. $S = 1$
 - A. Eigenvalue problem for $S = 1$
 - B. Magnetic susceptibility with the quenching of the spin angular momentum
 - C. Mathematica program: energy diagram of the spin Hamiltonian with $S = 1$ in the presence of magnetic field (the general case)
 - 12.3 $S = 3/2$
 - A. Simple case with $\varepsilon = 0$ and $\delta > 0$
 - B. Kramers doublet
 - C. Mathematica program: energy diagram of the spin Hamiltonian with $S = 3/2$ in the presence of magnetic field
 - 12.4 Energy diagram for $S = 2$
 - 12.5 $S = 5/2$
 - A. Simple case for $S = 5/2$
 - B. Mathematica program for $S = 5/2$ (general case)
 - 13. Spin Hamiltonian of Fe^{2+} and Co^{2+} in the trigonal crystal field
 - 13.1 Fe^{2+}
 - A. Energy diagram
 - B. Spin Hamiltonian with fictitious spin $s = 1$.
 - C. Mathematica program: energy diagram of Fe^{2+} in the trigonal field
 - 13.2 Co^{2+}
 - A. Energy diagram of Co^{2+}
 - B. Spin Hamiltonian with fictitious spin $s = 1/2$
 - C. Mathematica program: energy diagram of Co^{2+} in the trigonal field
 - 14. Conclusion
- References
- Appendix

Note: $1 \text{ meV} = 11.6045 \text{ K} = 8.06548 \text{ cm}^{-1} = 0.241797 \text{ THz}$

1. Introduction: a brief history on the modern magnetism

Magnetism is inseparable from quantum mechanics, for a strictly classical system in thermal equilibrium can display no magnetic moment, even in a magnetic field (Kittel³). The magnetism is essentially the quantum phenomenon and is a property, reflecting the feature of quantum mechanics. In his talk titled the quantum mechanics, key to understanding magnetism (the Nobel lecture, December 8, 1977), Van Vleck¹ pointed out that modern theories of magnetism have roots in two distinct traditions of theoretical developments. The first outstanding early attempt to understand magnetism at the atomic level was provided by the semi-empirical theories of Langevin and Weiss. These theories were able to explain experimental results on the magnetic properties of materials. Langevin

assumed that an atomic or molecular magnet carries a permanent magnetic moment. He was quantizing the system without realizing it. If one applies classical dynamics and statistical mechanics consistently, one finds that the diamagnetic and paramagnetic contributions to the magnetic susceptibility exactly cancel. Thus there should be no magnetism. The break-through in understanding of magnetic phenomena at the atomic level occurred in 1913, when Niels Bohr introduced the significant concept of the quantization of the orbital angular momentum, as a part of his remarkable theory of the hydrogen spectrum. The quantization of electron orbits implied the existence of an elementary magnetic moment, the Bohr magneton. In 1922, Stern and Gerlach experimentally verified the quantized orbital angular momentum and hence the orbital magnetic moment.

The advent of quantum mechanics in 1926 furnished at last the key to the quantitative understanding of magnetism, (i) the discovery of the matrix form of quantum mechanics by Heisenberg and Born, (ii) the alternative but equivalent wave mechanical form by de Broglie and Schrödinger, and (iii) the introduction of electron spin by Uhlenbeck and Goulsmit. A quantum mechanics without spin and the Pauli's exclusion principle would not have been able to understand even the structure of the periodic table or most magnetic phenomena. Originally spin was a sort of the appendage to the mathematical framework, but in 1928, Dirac synthesized everything in his remarkable four first order simultaneous equations which is relativistically invariant under the Lorentz transformation. The electron spin and the factor of two came naturally out of the calculation. In 1928, Heisenberg has shown how the previously obscure Weiss molecular field could be attributed to a quantum mechanical exchange effect, arising from the Pauli's exclusion principle that no two electrons occupy the same state. The forces of interaction between neighboring atoms give rise to a exchange coupling between unpaired spinning electron. This leads to a scalar isotropic interaction of two spins with an exchange interaction constant (see the book written by Hoddeson et al.⁷, "Out of the Crystal Maze" for more detail of the above review).

In the early 1930's there appeared two major textbooks devoted to the topics of magnetism, Van Vleck's *Theory of Electric and Magnetic Susceptibilities* (1932)⁸ and Stoner's *Magnetism and Matter* (1934).⁹ These are considered to be the best classic texts in modern magnetism.

John H. Van Vleck (born March 13, 1899, Middletown, Connecticut, died Oct. 27, 1980, Cambridge, Massachusetts.) American physicist and mathematician who shared the Nobel Prize for Physics in 1977 with Philip W. Anderson and Nevill F. Mott. The prize honoured Van Vleck's contributions to the understanding of the behavior of electrons in magnetic, non-crystalline solid materials. Educated at the University of Wisconsin, Madison, and at Harvard University, where he received his Ph.D. in 1922, He developed during the early 1930s the first fully articulated quantum mechanical theory of magnetism. Later he was a chief architect of the ligand field theory of molecular bonding.

2. Fundamentals

A. Angular momentum and magnetic momentum of one electron

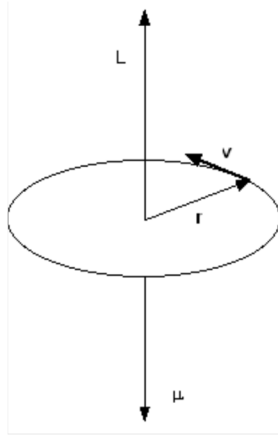


Fig.1 Orbital (circular) motion of electron with mass m and a charge $-e$. The direction of orbital angular momentum L is perpendicular to the plane of the motion (x - y plane).

The orbital angular momentum of an electron (charge $-e$ and mass m) L is defined by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (m\mathbf{v}), \text{ or } L_z = mvr. \quad (2.1)$$

According to the de Broglie relation, we have

$$p(2\pi r) = \frac{h}{\lambda} 2\pi r = nh, \quad (2.2)$$

where $p (= mv)$ is the momentum ($p = \frac{h}{\lambda}$), n is integer, h is the Planck constant, and λ is the wavelength.

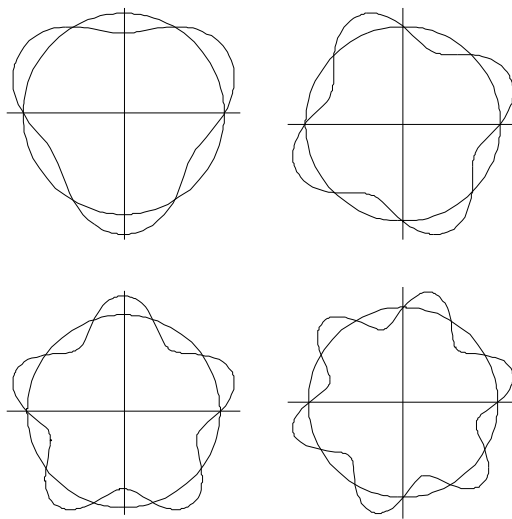


Fig.2 Acceptable wave on the ring (circular orbit). The circumference should be equal to the integer n ($=1, 2, 3, \dots$) times the de Broglie wavelength λ .

The picture of fitting the de Broglie waves onto a circle makes clear the reason why the orbital angular momentum is quantized. Only integral numbers of wavelengths can be fitted. Otherwise, there would be destructive interference between waves on successive cycles of the ring.

Then the angular momentum L_z is described by

$$L_z = pr = mvr = \frac{nh}{2\pi} = n\hbar. \quad (2.3)$$

The magnetic moment of the electron is given by

$$\mu_z = \frac{1}{c} I_\theta A, \quad (2.4)$$

where c is the velocity of light, $A = \pi r^2$ is the are of the electron orbit, and I_θ is the current due to the circular motion of the electron. Note that the direction of the current is opposite to that of the velocity because of the negative charge of the electron. The current I_θ is given by

$$I_\theta = -\frac{e}{T} = -\frac{e}{(2\pi r/v)} = -\frac{ev}{2\pi r}, \quad (2.5)$$

where T is the period of the circular motion. Then the magnetic moment is derived as

$$\mu_z = \frac{1}{c} I_\theta A = -\frac{evr}{2c} = -\frac{e}{2mc} L_z = -\frac{e\hbar}{2mc} \frac{L_z}{\hbar} = -\frac{\mu_B}{\hbar} L_z \quad (e > 0), \quad (2.6)$$

where $\mu_B (= \frac{e\hbar}{2mc})$ is the Bohr magneton. $\mu_B = 9.27400915 \times 10^{-21}$ emu. emu=erg/Oe. Since

$L_z = n\hbar$, the magnitude of orbital magnetic moment is $n\mu_B$.

The spin magnetic moment is given by

$$\mu_s = -\frac{2\mu_B}{\hbar} \mathbf{S}, \quad (2.7)$$

where \mathbf{S} is the spin angular momentum.

In quantum mechanics, the above equation is described by

$$\hat{\mu} = -\frac{2\mu_B}{\hbar} \hat{S}, \quad (2.8)$$

using operators (Dirac). When $\hat{S} = \frac{\hbar}{2} \hat{\sigma}$, we have $\hat{\mu} = -\mu_B \hat{\sigma}$. The spin angular momentum is described by the Pauli matrices (operators)

$$\hat{S}_x = \frac{\hbar}{2} \hat{\sigma}_x, \hat{S}_y = \frac{\hbar}{2} \hat{\sigma}_y, \hat{S}_z = \frac{\hbar}{2} \hat{\sigma}_z. \quad (2.9)$$

Using the basis,

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (2.10)$$

we have

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.11)$$

The commutation relations are valid;

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z, [\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x, [\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y. \quad (2.12)$$

The resultant magnetic moment of an electron is given by

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}). \quad (2.13)$$

B. Periodic table of iron group elements

The Pauli principle produces any two electrons being in the same state (i.e., having the set of (n, l, m_l, m_s)).

For fixed n , $l = n-1, n-2, \dots, 2, 1$

$$m_l = l, l-1, \dots, -l \quad (2l+1).$$

Therefore there are n^2 states for a given n .

$$\sum_{l=0}^{n-1} (2l+1) \quad // \text{Simplify}$$

$$n^2$$

There are two values for m_s ($= \pm 1/2$).

Thus, corresponding to any value of n , there are $2n^2$ states.

K shell

n	l	m	s	m_s	
1	0	0	1/2	$\pm 1/2$	$(1s)^2$

L shell						
n	l	m	s	m_s		
2	0	0	1/2	$\pm 1/2$	$(2s)^2$	
2	1	1,0,-1	1/2	$\pm 1/2$	$(2p)^6$	
M shell						
n	l	m	s	m_s		
3	0	0	1/2	$\pm 1/2$	$(3s)^2$	
3	1	1,0,-1	1/2	$\pm 1/2$	$(3p)^6$	
3	2	2,1,0,-1,-2	1/2	$\pm 1/2$	$(3d)^{10}$	
N shell						
n	l	m	s	m_s		
4	0	0	1/2	$\pm 1/2$	$(4s)^2$	
4	1	1,0,-1	1/2	$\pm 1/2$	$(4p)^6$	
4	2	2,1,0,-1,-2	1/2	$\pm 1/2$	$(4d)^{10}$	
4	3	3,2,1,0,-1,-2,-3	1/2	$\pm 1/2$	$(4f)^{14}$	

$$(1s)^2|(2s)^2(2p)^6|(3s)^2(3p)^6(3d)^{10}|(4s)^2(4p)^6(4d)^{10}(4f)^{14}|(5s)^2(5p)^6((5d)^{10}) \dots$$

Iron-group elements:

Ti^{3+}, V^{4+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^1$
V^{3+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^2$
Cr^{3+}, V^{2+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^3$
Cr^{2+}, Mn^{3+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^4$
Mn^{2+}, Fe^{3+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^5$
Fe^{2+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^6$
Co^{2+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^7$
Ni^{2+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^8$
Cu^{2+}	$(1s)^2 (2s)^2(2p)^6 (3s)^2(3p)^6 (3d)^9$

Atoms with filled n shells have a total angular momentum and a total spin of zero. Electrons exterior these closed shells are called valence electrons.

C. Magnetic moment of atom

We consider an isolated atom with incomplete shell of electrons. The orbital angular momentum L and spin angular momentum S are given by

$$L = L_1 + L_2 + L_3 + \dots, \quad S = S_1 + S_2 + S_3 + \dots \quad (2.14)$$

The total angular momentum J is defined by

$$J = L + S. \quad (2.15)$$

The total magnetic moment μ is given by

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}). \quad (2.16)$$

The Landé g-factor is defined by

$$\boldsymbol{\mu}_J = -\frac{g_J \mu_B}{\hbar} \mathbf{J}, \quad (2.17)$$

where

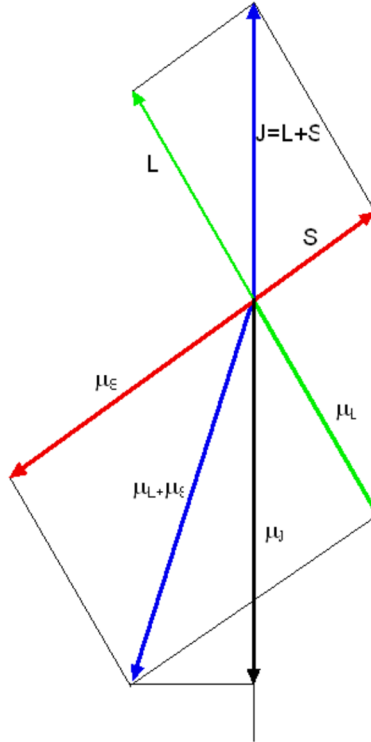


Fig.3 Basic classical vector model of orbital angular momentum (\mathbf{L}), spin angular momentum (\mathbf{S}), orbital magnetic moment ($\boldsymbol{\mu}_L$), and spin magnetic moment ($\boldsymbol{\mu}_S$). $\mathbf{J} (= \mathbf{L} + \mathbf{S})$ is the total angular momentum. $\boldsymbol{\mu}_J$ is the component of the total magnetic moment ($\boldsymbol{\mu}_L + \boldsymbol{\mu}_S$) along the direction ($-\mathbf{J}$).

Suppose that

$$\mathbf{L} = a\mathbf{J} + \mathbf{L}_\perp \quad (2.18a)$$

$$\mathbf{S} = b\mathbf{J} + \mathbf{S}_\perp, \quad (2.19b)$$

where a and b are constants, and the vectors \mathbf{S}_\perp and \mathbf{L}_\perp are perpendicular to \mathbf{J} . Here we have the relation $a + b = 1$, and $\mathbf{L}_\perp + \mathbf{S}_\perp = 0$. The values of a and b are determined as follows.

$$a = \frac{\mathbf{J} \cdot \mathbf{L}}{\mathbf{J}^2}, \quad b = \frac{\mathbf{J} \cdot \mathbf{S}}{\mathbf{J}^2}. \quad (2.19)$$

Here we note that

$$\begin{aligned} \mathbf{J} \cdot \mathbf{S} &= (\mathbf{L} + \mathbf{S}) \cdot \mathbf{S} \\ &= \mathbf{S}^2 + \mathbf{L} \cdot \mathbf{S}, \\ &= \mathbf{S}^2 + \frac{\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2}{2} = \frac{\mathbf{J}^2 - \mathbf{L}^2 + \mathbf{S}^2}{2}, \end{aligned} \quad (2.20)$$

or

$$\mathbf{J} \cdot \mathbf{S} = \frac{\mathbf{J}^2 - \mathbf{L}^2 + \mathbf{S}^2}{2} = \frac{\hbar^2}{2} [J(J+1) - L(L+1) + S(S+1)], \quad (2.21)$$

using the average in quantum mechanics. The total magnetic moment $\boldsymbol{\mu}$ is

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) = -\frac{\mu_B}{\hbar} [(a+2b)\mathbf{J} + (L_{\perp} + 2S_{\perp})]. \quad (2.22)$$

Thus we have

$$\boldsymbol{\mu}_J = -\frac{\mu_B}{\hbar} (a+2b)\mathbf{J} = -\frac{\mu_B}{\hbar} (1+b)\mathbf{J} = -\frac{g_J \mu_B}{\hbar} \mathbf{J}, \quad (2.23)$$

with

$$g_J = 1 + b = 1 + \frac{\mathbf{J} \cdot \mathbf{S}}{\mathbf{J}^2} = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \quad (2.24)$$

((Note))

The spin component is given by

$$\mathbf{S} = b\mathbf{J} + \mathbf{S}_{\perp} = (g_J - 1)\mathbf{J} + \mathbf{S}_{\perp}, \quad (2.25)$$

with $b = g_J - 1$. The de Gennes factor is defined by

$$\frac{(g_J - 1)^2 \mathbf{J}^2}{\hbar^2} = (g_J - 1)^2 J(J+1). \quad (2.26)$$

In ions with strong spin-orbit coupling the spin is not a good quantum number, but rather the total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The spin operator is described by

$$\mathbf{S} = (g_J - 1)\mathbf{J}. \quad (2.27)$$

D. Spin-orbit interaction in an electron around the nucleus

The electron has an orbital motion around the nucleus. This also implies that the nucleus has an orbital motion around the electron. The motion of nucleus produces an orbital current. From the Biot-Savart's law, it generates a magnetic field on the electron.

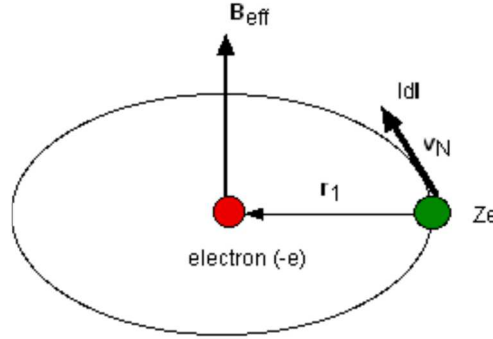


Fig.4 Simple model for the spin-orbit interaction. The orbital current due to the circular motion of the nucleus (with velocity \mathbf{v}_N and charge Ze) produces an magnetic field at the center where the electron is located.

The current I due to the movement of nucleus (charge Ze , $e > 0$) is given by

$$Idl = Ze\mathbf{v}_N, \quad (2.28)$$

where \mathbf{v}_N is the velocity of the nucleus and $\frac{dl}{dt} = \mathbf{v}_N$. Note that

$$Idl = \frac{\Delta q}{\Delta t} dl = \Delta q \frac{dl}{dt} = Ze\mathbf{v}_N. \quad (2.29)$$

The effective magnetic field at the electron at the origin is

$$\mathbf{B}_{eff} = \frac{I}{c} \frac{d\mathbf{l} \times \mathbf{r}_1}{r_1^3}, \quad \mathbf{v}_N = v\mathbf{e}_\theta, \quad (2.30)$$

where v is the velocity of the electron. Then we have

$$\mathbf{B}_{eff} = \frac{Ze}{c} \frac{\mathbf{v}_N \times \mathbf{r}_1}{r_1^3} = \frac{Ze}{c} \frac{v\mathbf{e}_\theta \times \mathbf{r}_1}{r_1^3}. \quad (2.31)$$

Since $\mathbf{r}_1 = -\mathbf{r}$, \mathbf{B}_{eff} can be rewritten as

$$\mathbf{B}_{eff} = \frac{Ze}{c} \frac{\mathbf{v}_N \times \mathbf{r}_1}{r_1^3} = \frac{Ze}{c} \frac{v\mathbf{e}_\theta \times \mathbf{r}_1}{r_1^3}, \quad (2.32)$$

or

$$\mathbf{B}_{eff} = -\frac{Ze}{c} \frac{v\mathbf{e}_\theta \times \mathbf{r}}{r^3} = \frac{Zev}{c} \frac{\mathbf{e}_\theta \times \mathbf{r}}{r^2} = \frac{Zev}{c} \frac{\mathbf{e}_z}{r^2} = \frac{Zev}{c} \frac{\mathbf{e}_z}{r^2} = \frac{Zemv}{mcr^2} \mathbf{e}_z. \quad (2.33)$$

The Coulomb potential energy is given by

$$V_c(r) = -\frac{Ze^2}{r}, \quad \frac{dV_c(r)}{dr} = \frac{Ze^2}{r^2}. \quad (2.34)$$

Thus we have

$$\begin{aligned} \mathbf{B}_{eff} &= \frac{Zemrv}{mcr^3} \mathbf{e}_z = \frac{Ze^2 mrv}{mcer^3} \mathbf{e}_z = \frac{Ze^2 m_0rv}{mcer^2} \mathbf{e}_z \\ &= \frac{1}{mcer} \frac{Ze^2}{r^2} m_0rv \mathbf{e}_z = \frac{1}{mcer} \frac{dV_c(r)}{dr} L_z \mathbf{e}_z \end{aligned} \quad (2.35)$$

or

$$\mathbf{B}_{eff} = \frac{1}{mce} \frac{1}{r} \frac{dV_c(r)}{dr} L_z \mathbf{e}_z, \quad (2.36)$$

where L_z is the z -component of the orbital angular momentum, $L_z = mvr$.

The spin magnetic moment is given by

$$\boldsymbol{\mu}_s = -\frac{2\mu_B}{\hbar} \mathbf{S}. \quad (2.37)$$

The Zeeman energy is given by

$$\begin{aligned} H_{LS} &= -\frac{1}{2} \boldsymbol{\mu}_s \cdot \mathbf{B}_{eff} \\ &= -\frac{1}{2} \left(-\frac{2\mu_B}{\hbar} \mathbf{S} \right) \cdot \left(\frac{1}{mce} \frac{1}{r} \frac{dV_c(r)}{dr} \mathbf{L} \right) \\ &= \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV_c(r)}{dr} \mathbf{S} \cdot \mathbf{L} = \xi(\mathbf{S} \cdot \mathbf{L}) \end{aligned} \quad (2.38)$$

((Thomas correction))

Thomas factor 1/2, which represents an additional relativistic effect due to the acceleration of the electron. The electron spin, magnetic moment, and spin-orbit interaction can be derived directly from the Dirac relativistic electron theory. The Thomas factor is built in the expression.

$$H_{LS} = \xi \mathbf{S} \cdot \mathbf{L}, \quad (2.39)$$

with

$$\xi = \left\langle \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV_c(r)}{dr} \right\rangle = \frac{1}{2} Z \left(\frac{e}{mc} \right)^2 \left\langle \frac{1}{r^3} \right\rangle_{av}. \quad (2.40)$$

When we use the formula

$$\left\langle r^{-3} \right\rangle = \frac{Z^3}{n^4 a_0^3 l(l+1/2)(l+1)}, \quad (2.41)$$

the spin-orbit interaction constant ξ is described by

$$\xi = \frac{e^2 Z^4}{2m^2 c^2 n^4 a_0^3 l(l+1/2)(l+1)} = \frac{me^8 Z^4}{2c^2 n^4 \hbar^6 l(l+1/2)(l+1)}, \quad (2.42)$$

where

$$a_0 = \frac{\hbar^2}{me^2} = 0.52917720859 \text{ \AA}. \quad (2.43)$$

(Bohr radius, from NIST physics constants)

The energy level (negative) is given by

$$|E_n| = \frac{Z^2}{n^2} \frac{me^4}{2\hbar^2} = \frac{Z^2 e^2}{2n^2 a_0}. \quad (2.44)$$

The ratio $\hbar^2 \xi / |E_n|$ is

$$\frac{\hbar^2 \xi}{|E_n|} = \frac{e^4 Z^2}{c^2 n^2 \hbar^2 l(l+1/2)(l+1)} = \frac{(\alpha Z)^2}{n^2} \frac{1}{l(l+1/2)(l+1)}, \quad (2.45)$$

with

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.037}. \quad (2.46)$$

((Note)) For $l = 0$ the spin-orbit interaction vanishes and therefore $\xi = 0$ in this case.

3. Hund's rule

3.1. Electron states in the atom

For a given l , the number m takes $2l + 1$ values. The number s is restricted to only two values $\pm 1/2$. Hence there are altogether $2(2l+1)$ different states with the same n and l . These states are said to be equivalent.

According to Pauli's principle, there can be only one electron in each such state. Thus at most $2(2l+1)$ electrons in an atom can simultaneously have the same n and l . Hund's rule is known concerning the relative position of levels with the same configuration but different L and S .

Hund's first law

- (1) The maximum values of the total spin S allowed by the exclusion principle.

Hund's second law

- (2) The maximum values of the total orbital angular momentum L consistent with this value of S .

Hund's third law

- (i) $J = |L - S|$ for less than half full (spin-orbit interaction, the discussion will be made later)
 (ii) $J = L + S$ for more than half full (spin-orbit interaction).

3.2. The electron configuration $(3d)^n$ ($l = 2, n = 1 - 10$)

A d shell corresponds to $l = 2$, with five values of m_l . Multiplying this by 2 for the spin states gives a total of 10. Then the configuration $(3d)^{10}$ represents a full shell. It is non-degenerate, and the state is 1S_0 . This is a general rule for a full shell. It follows because each of electrons must have a different pair of m_l and m_s values.

$(3d)^1$: Ti^{3+}, V^{4+}

$^2D_{3/2}$ (ground state)

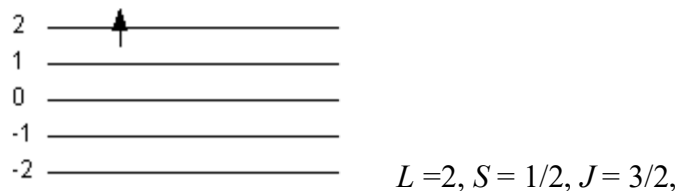


Fig.5(a) Hund's law for the $(3d)^1$ electron configuration.

$(3d)^2$: V^{3+}
 3F_2

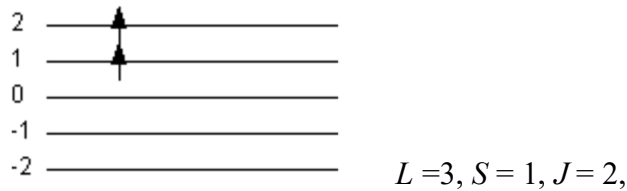


Fig.5(b) Hund's law for the $(3d)^2$ electron configuration.

$(3d)^3$: $\text{Cr}^{3+}, \text{V}^{2+}$
 ${}^4\text{F}_{3/2}$

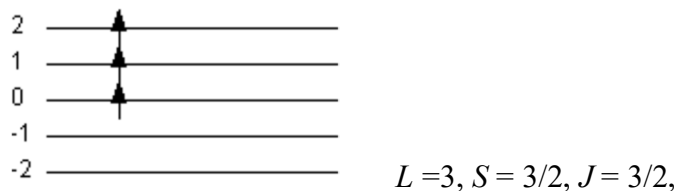


Fig.5(c) Hund's law for the $(3d)^3$ electron configuration.

$(3d)^4$: $\text{Cr}^{2+}, \text{Mn}^{3+}$
 ${}^5\text{D}_0$

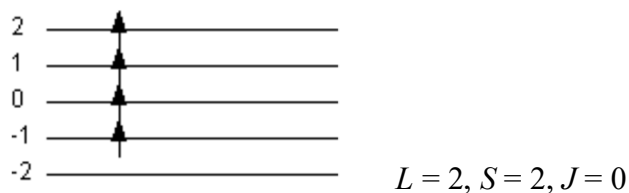


Fig.5(d) Hund's law for the $(3d)^4$ electron configuration.

$(3d)^5$: $\text{Fe}^{3+}, \text{Mn}^{2+}$
 ${}^6\text{S}_{5/2}$

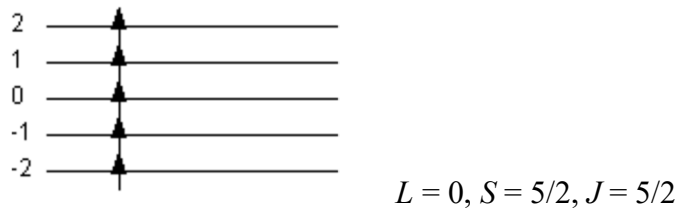


Fig.5(e) Hund's law for the $(3d)^5$ electron configuration.

$(3d)^6$: Fe^{2+}
 ${}^5\text{D}_4$

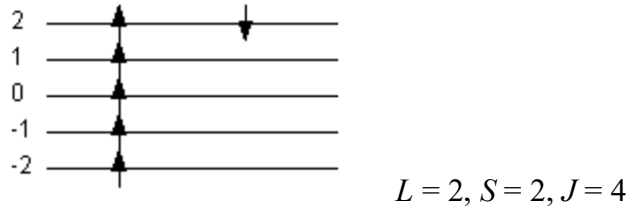


Fig.5(f) Hund's law for the $(3d)^6$ electron configuration.

$(3d)^7$: Co^{2+}
 $^4F_{9/2}$

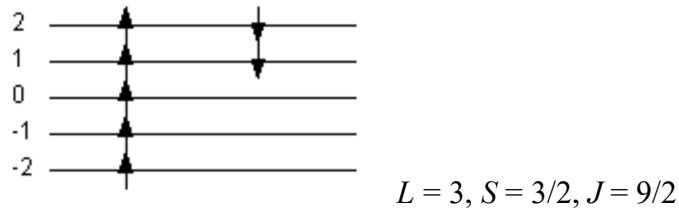


Fig.5(g) Hund's law for the $(3d)^7$ electron configuration.

$(3d)^8$: Ni^{2+}
 3F_4

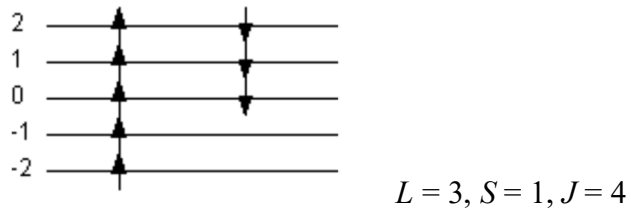


Fig.5(h) Hund's law for the $(3d)^8$ electron configuration.

$(3d)^9$: Cu^{2+}
 $^2D_{5/2}$

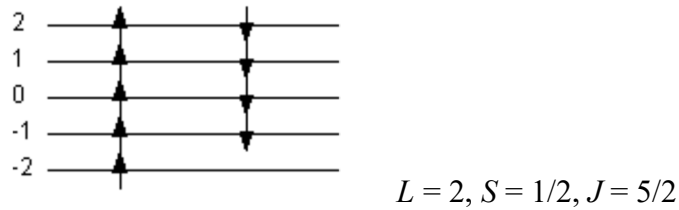


Fig.5(i) Hund's law for the $(3d)^9$ electron configuration.

(3d)⁹

This configuration represents a set of electrons one short of a full shell. Since a full shell has zero angular momentum (both orbital and spin), it follows that if one electron is removed from a full shell, the spin angular momentum of the remainder are minus those of the one that was removed. So the L , S , and J values of remainder are the same as if there were only one electron in the shell.

(3d)¹⁰

A d shell corresponds to $l = 2$, with five values of m_l . Multiplying this by two for the spin states gives 10. Thus the configuration (3d)¹⁰ represents a full shell. $L = 0$. $S = 0$. $J = 0$.

3.3. Spin orbit interaction of isolated atom

The total spin-orbit interaction is given by

$$H_{LS} = \xi \sum_i \mathbf{S}_i \cdot \mathbf{L}_i = \lambda \mathbf{L} \cdot \mathbf{S}, \quad (3.1)$$

where \mathbf{S}_i and \mathbf{L}_i are the spin and orbital angular momenta, respectively (Wigner-Eckart theorem). We take an average of both sides.

$$\xi \sum_i m_i^S \cdot m_i^L = \lambda M_L \cdot M_S, \quad (3.2)$$

where $M_L = L$, $M_S = S$ which are determined from the Hund rules (1) and (2). For simplicity, we now consider the ground state of the (3d)ⁿ electron configuration.



Fig.6 Hund's law for (3d)³ and (3d)⁷ electron configurations.

The value of J can have $J = L+S, L+S-1, \dots, |L-S|$.

When $\lambda > 0$, the energy becomes low for the smallest value of J ($= |L-S|$) (antiparallel).

When $\lambda < 0$, the energy becomes low for the largest value of J ($= L+S$) (parallel).

(1) Less than half case ($n < 2l+1$)

$$\xi \frac{1}{2} \cdot L = \lambda L \cdot S, \quad (3.3)$$

where $S = n/2$. Then we have $\lambda = \frac{\xi}{2S} = \frac{\xi}{n} > 0$, which favors $J = |L-S|$.

(2) More than half case ($n > 2l+1$)

$$\xi\left(\frac{1}{2} \cdot 0 - \frac{1}{2}L\right) = \lambda L \cdot S, \text{ or } \lambda = -\frac{\xi}{2(2l+1) - n} < 0, \quad (3.4)$$

where

$$S = \frac{1}{2}(2l+1) - \frac{1}{2}[n - (2l+1)] = (2l+1) - \frac{n}{2}.$$

This condition favors $J = L+S$. The third Hund' rule is a consequence of the sign of the spin-orbit interaction.

4. Crystal field

4.1 Overview

Rare-earth: The $4f$ shell responsible for paramagnetism lies deep inside the ions, within the $5s$ and $5p$ shells. J is a good quantum number. ($L-S$ coupling \gg crystal field).

Iron group: The $3d$ shell responsible for paramagnetism is the outermost shell. The $3d$ shell experiences the intense inhomogeneous electric field produced by neighboring ions. The inhomogeneous electric field is called the crystal field. (Crystal field $\gg L-S$ coupling).

Two major effect of the crystal field

(i) The coupling of L and S is largely broken up. So that the states are no longer specified by their J values.

$(2L+1)(2S+1)$ degeneracy \rightarrow orbital splitting due to the crystal field (degeneracy $2S+1$) $\rightarrow L-S$ coupling

(ii) $2L+1$ sublevels belonging to a given L , which are degenerate in the free ion may now be split by the crystal field. The quenching of the orbital angular momentum.

$(2J+1)$ degeneracy (Hund's rules) $\rightarrow L-S$ coupling \rightarrow crystal field.

We note that there are many excellent textbooks,^{10,14} review articles,¹⁵ and original papers^{16,17} on the ligand field theory, including Griffiths (The Theory of Transition-Metal Ions),¹⁰ Abraham and Bleaney (Electron Paramagnetic Resonance of Transition Ions),¹¹ Sugano et al. (Multiplets of Transition-Metal Ions in Crystals),¹² Inui et al. (Group Theory and Its Applications in Physics),¹³ and Ballhausen (Introduction to Ligand Field Theory).¹⁴

4.2 Series expansion of the crystal field

Ions M at the origin $(0, 0, 0)$ are surrounded by six negative ions X with charge $-Ze$ ($e > 0$), which are located on the x -, y -, and z -axes at the coordinates $(\pm a, 0, 0)$, $(0, \pm b, 0)$, and $(0, 0, \pm c)$, where a , b , and c are distances.

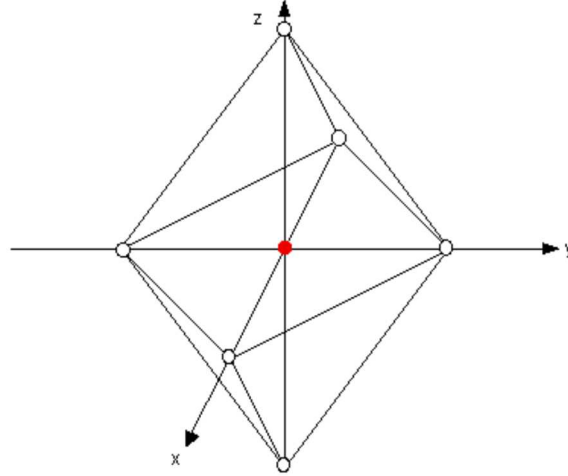


Fig.7 Crystal structure of octahedral and tetragonal structures. A magnetic ion (red solid circle) with one electron (a charge $-e$) is located at the origin. Six ions (open circles, each ion has a $-Ze$ charges) are located on the x -, y -, and z -axes at the coordinates $(\pm a, 0, 0)$, $(0, \pm b, 0)$, and $(0, 0, \pm c)$, where a , b , and c are distances. $a = b = c$ for the octahedral structure. $a = b \neq c$ for the tetragonal structure.

We consider an electrostatic potential energy of an electron (a charge $-e$, typically $2p$, $3d$, or $4f$ electrons) of the M ion, due to the Coulomb field (ligand), defined by

$$V(\mathbf{r}) = Ze^2 \left[\frac{1}{\sqrt{(x-a)^2 + y^2 + z^2}} + \frac{1}{\sqrt{(x+a)^2 + y^2 + z^2}} + \frac{1}{\sqrt{x^2 + (y-b)^2 + z^2}} \right. \\ \left. + \frac{1}{\sqrt{x^2 + (y+b)^2 + z^2}} + \frac{1}{\sqrt{x^2 + y^2 + (z-c)^2}} + \frac{1}{\sqrt{x^2 + y^2 + (z+c)^2}} \right] \quad (4.1)$$

where $a = b = c$ for the orthorhombic (cubic) field and $a = b (\neq c)$ for the tetragonal field.

4.3 Mathematica program

We use the Mathematica to expand $V(r)$ around the origin in terms of the powers $x^p y^q z^r$ with the maximum of $p + q + r = n$

- (i) $n = 2$ for the $2p$ electrons.
- (ii) $n = 4$ for the $3d$ electrons,
- (iii) $n = 6$ for the $4f$ electrons.

Expansion of the Crystal field
Orthorhombic, orthogonal, tetragonal

Clear ["Global`*"];

$$\begin{aligned}
 Vc = & \frac{1}{\sqrt{(x-a)^2 + y^2 + z^2}} + \frac{1}{\sqrt{(x+a)^2 + y^2 + z^2}} + \frac{1}{\sqrt{(y-b)^2 + x^2 + z^2}} + \\
 & \frac{1}{\sqrt{(y+b)^2 + x^2 + z^2}} + \frac{1}{\sqrt{(z-c)^2 + y^2 + x^2}} + \frac{1}{\sqrt{(z+c)^2 + y^2 + x^2}} \\
 & \frac{1}{\sqrt{(-a+x)^2 + y^2 + z^2}} + \frac{1}{\sqrt{(a+x)^2 + y^2 + z^2}} + \frac{1}{\sqrt{x^2 + (-b+y)^2 + z^2}} + \\
 & \frac{1}{\sqrt{x^2 + (b+y)^2 + z^2}} + \frac{1}{\sqrt{x^2 + y^2 + (-c+z)^2}} + \frac{1}{\sqrt{x^2 + y^2 + (c+z)^2}}
 \end{aligned}$$

h[α_, β_] := If[0 ≤ α ≤ β, 1, 0];

General case (the highest order=4)

```

eq1 =
Series [Vc, {x, 0, 4}, {y, 0, 4}, {z, 0, 4}] //
FullSimplify [# , {a > 0, b > 0, c > 0}] & // Normal // Expand ;
eq12 = Sum [x^p y^q z^r Coefficient [x y z eq1, x^{p+1} y^{q+1} z^{r+1}]
h[p+q+r, 4], {p, 0, 4}, {q, 0, 4}, {r, 0, 4}]

```

$$\begin{aligned}
 & \frac{2}{a} + \frac{2}{b} + \frac{2}{c} + \frac{1}{2} \left(\frac{4}{a^3} - \frac{2}{b^3} - \frac{2}{c^3} \right) x^2 + \frac{1}{24} \left(\frac{48}{a^5} + \frac{18}{b^5} + \frac{18}{c^5} \right) x^4 + \\
 & \frac{1}{2} \left(-\frac{2}{a^3} + \frac{4}{b^3} - \frac{2}{c^3} \right) y^2 + \frac{1}{4} \left(-\frac{24}{a^5} - \frac{24}{b^5} + \frac{6}{c^5} \right) x^2 y^2 + \\
 & \frac{1}{24} \left(\frac{18}{a^5} + \frac{48}{b^5} + \frac{18}{c^5} \right) y^4 + \frac{1}{2} \left(-\frac{2}{a^3} - \frac{2}{b^3} + \frac{4}{c^3} \right) z^2 + \frac{1}{4} \left(-\frac{24}{a^5} + \frac{6}{b^5} - \frac{24}{c^5} \right) x^2 z^2 + \\
 & \frac{1}{4} \left(\frac{6}{a^5} - \frac{24}{b^5} - \frac{24}{c^5} \right) y^2 z^2 + \frac{1}{24} \left(\frac{18}{a^5} + \frac{18}{b^5} + \frac{48}{c^5} \right) z^4
 \end{aligned}$$

The crystal field of the d electrons

The case of a = b = c (orthorhombic (cubic))

eq2 = eq12 /. {b → a, c → a} // Expand

$$\frac{6}{a} + \frac{7x^4}{2a^5} - \frac{21x^2y^2}{2a^5} + \frac{7y^4}{2a^5} - \frac{21x^2z^2}{2a^5} - \frac{21y^2z^2}{2a^5} + \frac{7z^4}{2a^5}$$

This can be written as

$$\text{eq3} = \frac{6}{a} + \frac{35}{4a^5} \left(x^4 + y^4 + z^4 - \frac{3}{5} (x^2 + y^2 + z^2)^2 \right) // \text{Expand}$$

$$\frac{6}{a} + \frac{7x^4}{2a^5} - \frac{21x^2y^2}{2a^5} + \frac{7y^4}{2a^5} - \frac{21x^2z^2}{2a^5} - \frac{21y^2z^2}{2a^5} + \frac{7z^4}{2a^5}$$

$$\text{eq2} - \text{eq3} // \text{Simplify}$$

0

The case of a = b but not equal to c (tetragonal)

$$\text{eq4} = \text{eq12} /. \{b \rightarrow a\} // \text{Expand}$$

$$\frac{4}{a} + \frac{2}{c} + \frac{x^2}{a^3} - \frac{x^2}{c^3} + \frac{11x^4}{4a^5} + \frac{3x^4}{4c^5} + \frac{y^2}{a^3} - \frac{y^2}{c^3} - \frac{12x^2y^2}{a^5} + \frac{3x^2y^2}{2c^5} + \frac{11y^4}{4a^5} + \frac{3y^4}{4c^5} - \frac{2z^2}{a^3} + \frac{2z^2}{c^3} - \frac{9x^2z^2}{2a^5} - \frac{6x^2z^2}{c^5} - \frac{9y^2z^2}{2a^5} - \frac{6y^2z^2}{c^5} + \frac{3z^4}{2a^5} + \frac{2z^4}{c^5}$$

This can be written as

$$\text{eq5} = \frac{4}{a} + \frac{2}{c} + \left(\frac{1}{a^3} - \frac{1}{c^3} \right) (x^2 + y^2 - 2z^2) + \left(\frac{20}{4a^5} + \frac{15}{4c^5} \right) (x^4 + y^4 + z^4) - \left(\frac{5}{4a^5} - \frac{5}{4c^5} \right) (z^4 + 6x^2y^2) - \left(\frac{9}{4a^5} + \frac{12}{4c^5} \right) (x^2 + y^2 + z^2)^2 // \text{Expand}$$

$$\frac{4}{a} + \frac{2}{c} + \frac{x^2}{a^3} - \frac{x^2}{c^3} + \frac{11x^4}{4a^5} + \frac{3x^4}{4c^5} + \frac{y^2}{a^3} - \frac{y^2}{c^3} - \frac{12x^2y^2}{a^5} + \frac{3x^2y^2}{2c^5} + \frac{11y^4}{4a^5} + \frac{3y^4}{4c^5} - \frac{2z^2}{a^3} + \frac{2z^2}{c^3} - \frac{9x^2z^2}{2a^5} - \frac{6x^2z^2}{c^5} - \frac{9y^2z^2}{2a^5} - \frac{6y^2z^2}{c^5} + \frac{3z^4}{2a^5} + \frac{2z^4}{c^5}$$

$$\text{eq4} - \text{eq5} // \text{Simplify}$$

0

Crystal field for the p electrons (the highest order = 2)

a, b and c are different.

$$\text{eq13} = \text{Sum} [x^p y^q z^r \text{Coefficient} [x y z \text{eq1}, x^{p+1} y^{q+1} z^{r+1}] h[p+q+r, 2], \{p, 0, 4\}, \{q, 0, 4\}, \{r, 0, 4\}]$$

$$\frac{2}{a} + \frac{2}{b} + \frac{2}{c} + \frac{1}{2} \left(\frac{4}{a^3} - \frac{2}{b^3} - \frac{2}{c^3} \right) x^2 + \frac{1}{2} \left(-\frac{2}{a^3} + \frac{4}{b^3} - \frac{2}{c^3} \right) y^2 + \frac{1}{2} \left(-\frac{2}{a^3} - \frac{2}{b^3} + \frac{4}{c^3} \right) z^2$$

$$\text{A1} = \text{Coefficient} [\text{eq13}, x^2]; \text{B1} = \text{Coefficient} [\text{eq13}, y^2];$$

$$\text{C1} = \text{Coefficient} [\text{eq13}, z^2];$$

$$\text{A1} + \text{B1} + \text{C1} // \text{Simplify}$$

0

Crystal field for the f electrobns (the highest order = 6)

```

eq6 =
Series [Vc, {x, 0, 6}, {y, 0, 6}, {z, 0, 6}] //
FullSimplify [# , {a > 0, b > 0, c > 0}] & // Normal // Expand ;
eq61 = Sum [xp yq zr Coefficient [x y z eq6, xp+1 yq+1 zr+1]
h[p+q+r, 6] , {p, 0, 6}, {q, 0, 6}, {r, 0, 6}]

```

$$\begin{aligned}
& \frac{2}{a} + \frac{2}{b} + \frac{2}{c} + \frac{1}{2} \left(\frac{4}{a^3} - \frac{2}{b^3} - \frac{2}{c^3} \right) x^2 + \\
& \frac{1}{24} \left(\frac{48}{a^5} + \frac{18}{b^5} + \frac{18}{c^5} \right) x^4 + \frac{1}{720} \left(\frac{1440}{a^7} - \frac{450}{b^7} - \frac{450}{c^7} \right) x^6 + \\
& \frac{1}{2} \left(-\frac{2}{a^3} + \frac{4}{b^3} - \frac{2}{c^3} \right) y^2 + \frac{1}{4} \left(-\frac{24}{a^5} - \frac{24}{b^5} + \frac{6}{c^5} \right) x^2 y^2 + \\
& \frac{1}{48} \left(-\frac{720}{a^7} + \frac{540}{b^7} - \frac{90}{c^7} \right) x^4 y^2 + \frac{1}{24} \left(\frac{18}{a^5} + \frac{48}{b^5} + \frac{18}{c^5} \right) y^4 + \\
& \frac{1}{48} \left(\frac{540}{a^7} - \frac{720}{b^7} - \frac{90}{c^7} \right) x^2 y^4 + \frac{1}{720} \left(-\frac{450}{a^7} + \frac{1440}{b^7} - \frac{450}{c^7} \right) y^6 + \\
& \frac{1}{2} \left(-\frac{2}{a^3} - \frac{2}{b^3} + \frac{4}{c^3} \right) z^2 + \frac{1}{4} \left(-\frac{24}{a^5} + \frac{6}{b^5} - \frac{24}{c^5} \right) x^2 z^2 + \\
& \frac{1}{48} \left(-\frac{720}{a^7} - \frac{90}{b^7} + \frac{540}{c^7} \right) x^4 z^2 + \frac{1}{4} \left(\frac{6}{a^5} - \frac{24}{b^5} - \frac{24}{c^5} \right) y^2 z^2 + \\
& \frac{1}{8} \left(\frac{180}{a^7} + \frac{180}{b^7} + \frac{180}{c^7} \right) x^2 y^2 z^2 + \frac{1}{48} \left(-\frac{90}{a^7} - \frac{720}{b^7} + \frac{540}{c^7} \right) y^4 z^2 + \\
& \frac{1}{24} \left(\frac{18}{a^5} + \frac{18}{b^5} + \frac{48}{c^5} \right) z^4 + \frac{1}{48} \left(\frac{540}{a^7} - \frac{90}{b^7} - \frac{720}{c^7} \right) x^2 z^4 + \\
& \frac{1}{48} \left(-\frac{90}{a^7} + \frac{540}{b^7} - \frac{720}{c^7} \right) y^2 z^4 + \frac{1}{720} \left(-\frac{450}{a^7} - \frac{450}{b^7} + \frac{1440}{c^7} \right) z^6
\end{aligned}$$

Octahedral case (a=b=c)

```

eq7 = eq61 /. {b -> a, c -> a}

```

$$\begin{aligned}
& \frac{6}{a} + \frac{7x^4}{2a^5} + \frac{3x^6}{4a^7} - \frac{21x^2y^2}{2a^5} - \frac{45x^4y^2}{8a^7} + \frac{7y^4}{2a^5} - \\
& \frac{45x^2y^4}{8a^7} + \frac{3y^6}{4a^7} - \frac{21x^2z^2}{2a^5} - \frac{45x^4z^2}{8a^7} - \frac{21y^2z^2}{2a^5} + \\
& \frac{135x^2y^2z^2}{2a^7} - \frac{45y^4z^2}{8a^7} + \frac{7z^4}{2a^5} - \frac{45x^2z^4}{8a^7} - \frac{45y^2z^4}{8a^7} + \frac{3z^6}{4a^7}
\end{aligned}$$

Then we have the expansion of the crystal field with $n = 4$ for 3d electron.

(i) Potential in the case of different a , b , and c

$$\begin{aligned}
V(\mathbf{r}) = Ze^2 & \left[\frac{2}{a} + \frac{2}{b} + \frac{2}{c} \right. \\
& + \frac{1}{2} \left(\frac{4}{a^3} - \frac{2}{b^3} - \frac{2}{c^3} \right) x^2 + \frac{1}{2} \left(-\frac{2}{a^3} + \frac{4}{b^3} - \frac{2}{c^3} \right) y^2 + \frac{1}{2} \left(-\frac{2}{a^3} - \frac{2}{b^3} + \frac{4}{c^3} \right) z^2 \\
& + \frac{1}{4} \left(\frac{8}{a^5} + \frac{3}{b^5} + \frac{3}{c^5} \right) x^4 + \frac{1}{4} \left(\frac{3}{a^5} + \frac{8}{b^5} + \frac{3}{c^5} \right) y^4 + \frac{1}{4} \left(\frac{3}{a^5} + \frac{3}{b^5} + \frac{8}{c^5} \right) z^4 \\
& \left. + \frac{3}{2} \left(-\frac{4}{a^5} - \frac{4}{b^5} + \frac{1}{c^5} \right) x^2 y^2 + \frac{3}{2} \left(\frac{1}{a^5} - \frac{4}{b^5} - \frac{4}{c^5} \right) y^2 z^2 + \frac{3}{2} \left(-\frac{4}{a^5} + \frac{1}{b^5} - \frac{4}{c^5} \right) z^2 x^2 \right]
\end{aligned} \tag{4.2}$$

(ii) Potential in the case of $a = b$, but c being different from a and b (tetragonal field)

$$\begin{aligned}
V(\mathbf{r}) = Ze^2 & \left[\frac{4}{a} + \frac{2}{c} + \left(\frac{1}{a^3} - \frac{1}{c^3} \right) (x^2 + y^2 - 2z^2) + \frac{5}{4} \left(\frac{4}{a^5} + \frac{3}{c^5} \right) (x^4 + y^4 + z^4) \right. \\
& \left. - \frac{5}{4} \left(\frac{1}{a^5} - \frac{1}{c^5} \right) (z^4 + 6x^2 y^2) - \frac{3}{4} \left(\frac{3}{a^5} + \frac{4}{c^5} \right) r^4 \right].
\end{aligned} \tag{4.3}$$

where

$$r^2 = x^2 + y^2 + z^2.$$

(iii) Potential in the case of $a = b = c$ (orthorhombic field)

$$V(\mathbf{r}) = Ze^2 \left[\frac{6}{a} + \frac{7}{2a^5} (x^4 + y^4 + z^4) - \frac{21}{2a^5} (x^2 y^2 + y^2 z^2 + z^2 x^2) \right], \tag{4.4}$$

or

$$V(\mathbf{r}) = Ze^2 \left[\frac{6}{a} + \frac{35}{4a^5} (x^4 + y^4 + z^4 - \frac{3}{5} r^4) \right]. \tag{4.5}$$

5. p -electrons: quenching of the orbital angular momentum

5.1. $2p$ -electron wave functions

Frequently, the lowest orbital level, when split by a crystal field, is a singlet. Because of the large splitting, this is usually the only level populated. The orbital momentum is then said to be quenched, since it will make no contribution to the magnetic moment when a field is applied.

We now a simple model of quenching of the orbital angular momentum due to the crystal field. The electron configuration is given by $1s^2 2s^2 2p^1$ ($1s^2 2s^2$ has a closed shell). According to the Hund's law, we have $L = 1$ (degeneracy = $2L + 1 = 3$), $S = 1/2$ (degeneracy = $2S + 1 = 2$). Then the total degeneracy is $(2L + 1)(2S + 1) = 2 \times 3 = 6$. There is one p -electron. Suppose that this ion is surrounded by 6 negative ions located at $(\pm a, 0, 0)$, $(0, \pm b, 0)$, and $(0, 0, \pm c)$ with $a > b > c$. There are three wave functions: $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$ given by

$$\langle \mathbf{r} | p_x \rangle = xf(r), \quad \langle \mathbf{r} | p_y \rangle = yf(r), \quad \langle \mathbf{r} | p_z \rangle = zf(r), \quad (5.1)$$

with

$$\langle p_x | p_y \rangle = \langle p_y | p_z \rangle = \langle p_z | p_x \rangle = 0. \quad (5.2)$$

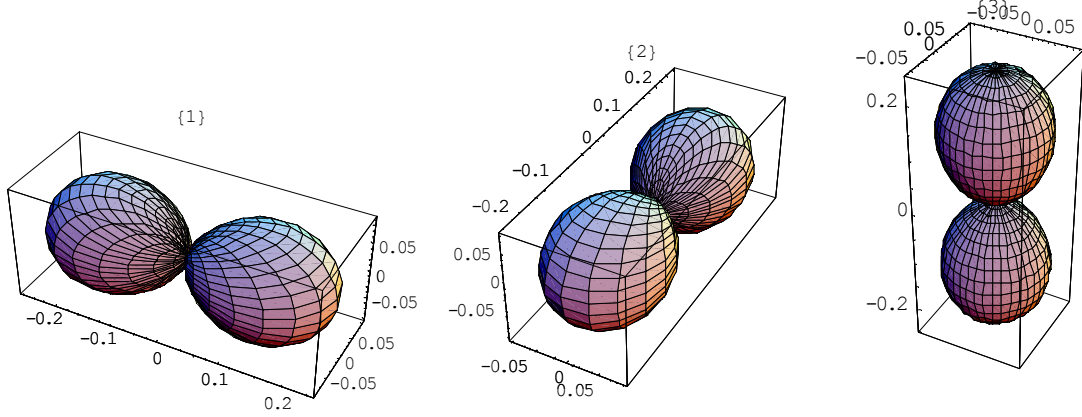


Fig.8 Angular parts of the wavefunctions for (1) $2p_x$, (2) $2p_y$, and (3) $2p_z$

$n = 2, l = 1$ ($2p$ electron)

$$R_{21}(r) = \frac{r \exp(-\frac{r}{2a_0})}{2\sqrt{6}a_0^{5/2}}, \quad (5.3)$$

$$\begin{aligned} Y_1^1(\theta, \phi) &= -\frac{1}{2} e^{i\phi} \sqrt{\frac{3}{2\pi}} \sin \theta \\ Y_1^0(\theta, \phi) &= \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta \\ Y_1^{-1}(\theta, \phi) &= \frac{1}{2} e^{-i\phi} \sqrt{\frac{3}{2\pi}} \sin \theta \end{aligned}, \quad (5.4)$$

$$\begin{aligned}
\langle \mathbf{r} | p_x \rangle &= \frac{1}{\sqrt{2}} [-Y_1^1(\theta, \phi) + Y_1^{-1}(\theta, \phi)] R_{21}(r) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \sin \theta \cos \phi R_{21}(r) = x \frac{1}{2} \sqrt{\frac{3}{\pi}} \frac{R_{21}(r)}{r} \\
\langle \mathbf{r} | p_y \rangle &= i \frac{1}{\sqrt{2}} [Y_1^1(\theta, \phi) + Y_1^{-1}(\theta, \phi)] R_{21}(r) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \sin \theta \sin \phi R_{21}(r) = y \frac{1}{2} \sqrt{\frac{3}{\pi}} \frac{R_{21}(r)}{r}, \\
\langle \mathbf{r} | p_z \rangle &= Y_1^0(\theta, \phi) R_{21}(r) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta = z \frac{1}{2} \sqrt{\frac{3}{\pi}} \frac{R_{21}(r)}{r}
\end{aligned} \tag{5.5}$$

with the radial wave function given by

$$f(r) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \frac{R_{21}(r)}{r} = \frac{1}{4\sqrt{2\pi}} \frac{\exp(-\frac{r}{2a_0})}{a_0^{5/2}}. \tag{5.6}$$

The energy is split because of the crystal field due to negative ions. $W_3 > W_2 > W_1$, because of Coulomb repulsion. Since $c < a < b$, one can find the longest Coulomb repulsion between negative ions and electron, for the z -axis, for y -axis, and for the x axis, in order.

5.2 2p electron in the octahedral field

The effect of negative ions is expressed by a static potential $V(\mathbf{r})$ satisfying the Laplace equation; $\nabla^2 V(\mathbf{r}) = 0$. This $V(\mathbf{r})$ is called the crystal field. Since $V(-\mathbf{r}) = V(\mathbf{r})$, $V(\mathbf{r})$ for the 2p electrons ($n = 2$) can be approximated as

$$V(\mathbf{r}) = -Ax^2 - By^2 + (A + B)z^2, \tag{5.7}$$

where $A > B > 0$ (see the above discussion for the derivation).

$$\begin{aligned}
A &= -\frac{Ze^2}{2} \left(\frac{4}{a^3} - \frac{2}{b^3} - \frac{2}{c^3} \right), \\
B &= -\frac{Ze^2}{2} \left(-\frac{2}{a^3} + \frac{4}{b^3} - \frac{2}{c^3} \right), \\
C &= \frac{Ze^2}{2} \left(-\frac{2}{a^3} - \frac{2}{b^3} + \frac{4}{c^3} \right) = A + B
\end{aligned} \tag{5.8}$$

$V(\mathbf{r})$ satisfies the Laplace equation; $\nabla^2 V(\mathbf{r}) = -2A - 2B + 2(A + B) = 0$

The matrix elements are calculated as (see the Mathematica)

$$\begin{aligned}
W_1 &= \langle p_x | \hat{V} | p_x \rangle = -24a_0^2 \pi A \\
W_2 &= \langle p_y | \hat{V} | p_y \rangle = -24a_0^2 \pi B \\
W_3 &= \langle p_z | \hat{V} | p_z \rangle = 24a_0^2 \pi (A + B)
\end{aligned} \quad (5.9)$$

Note that

$$\langle p_x | \hat{V} | p_y \rangle = 0, \quad \langle p_x | \hat{V} | p_z \rangle = 0, \quad \langle p_y | \hat{V} | p_z \rangle = 0, \dots, \quad (5.10)$$

The perturbation theory (quantum mechanics) can be applied to the ground states which are orbital-triplet states. As a result of the perturbation, these states are split into non-degenerate orbital-singlet states. Then the matrix of \hat{V} under the basis of $\{|p_x\rangle, |p_y\rangle, |p_z\rangle\}$ is diagonal, such that

$$\begin{pmatrix} \langle p_x | \hat{V} | p_x \rangle & \langle p_x | \hat{V} | p_y \rangle & \langle p_x | \hat{V} | p_z \rangle \\ \langle p_y | \hat{V} | p_x \rangle & \langle p_y | \hat{V} | p_y \rangle & \langle p_y | \hat{V} | p_z \rangle \\ \langle p_z | \hat{V} | p_x \rangle & \langle p_z | \hat{V} | p_y \rangle & \langle p_z | \hat{V} | p_z \rangle \end{pmatrix} = \begin{pmatrix} W_1 & 0 & 0 \\ 0 & W_2 & 0 \\ 0 & 0 & W_3 \end{pmatrix}.$$

In other words,

$$\hat{V} | p_x \rangle = W_1 | p_x \rangle, \quad \hat{V} | p_y \rangle = W_2 | p_y \rangle, \quad \hat{V} | p_z \rangle = W_3 | p_z \rangle$$

where the eigenkets are $|p_x\rangle$ with eigenvalue W_1 , $|p_y\rangle$ with eigenvalue W_2 , and $|p_z\rangle$ with eigenvalue W_3 . If $A \neq B$, then $W_1 \neq W_2$. As we expect, the degenerate ground state is separated into three orbital-singlet states; eigenstate $|p_x\rangle$ with the energy W_1 , eigenstate $|p_y\rangle$ with the energy W_2 , and eigenstate $|p_z\rangle$ with the energy W_3 .

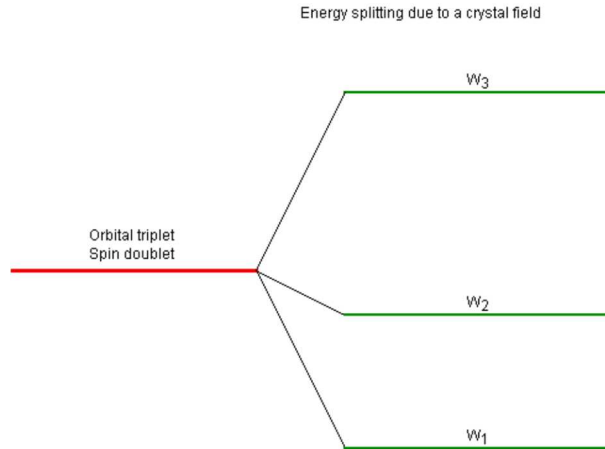


Fig.9 Schematic diagram of the energy splitting of $2p$ orbital under the tetragonal crystal field.

5.3. Quenching of orbital angular momentum

A. Orbital angular momentum (quantum mechanics)

The matrix element of the orbital angular momentum can be calculated as follows,

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \quad (5.13)$$

$$\begin{aligned} \hat{L}_z |p_x\rangle &= i\hbar |p_y\rangle, & \hat{L}_z |p_y\rangle &= -i\hbar |p_x\rangle, & \hat{L}_z |p_z\rangle &= 0 \\ \hat{L}_x |p_x\rangle &= 0, & \hat{L}_x |p_y\rangle &= i\hbar |p_z\rangle, & \hat{L}_x |p_z\rangle &= -i\hbar |p_y\rangle, \\ \hat{L}_y |p_x\rangle &= -i\hbar |p_z\rangle, & \hat{L}_y |p_y\rangle &= 0, & \hat{L}_y |p_z\rangle &= i\hbar |p_x\rangle \end{aligned} \quad (5.14)$$

Then we have

$$\begin{aligned} \langle p_x | \hat{L}_z | p_x \rangle &= \langle p_y | \hat{L}_z | p_y \rangle = \langle p_z | \hat{L}_z | p_z \rangle = 0 \\ \langle p_x | \hat{L}_x | p_x \rangle &= \langle p_y | \hat{L}_x | p_y \rangle = \langle p_z | \hat{L}_x | p_z \rangle = 0. \\ \langle p_x | \hat{L}_y | p_x \rangle &= \langle p_y | \hat{L}_y | p_y \rangle = \langle p_z | \hat{L}_y | p_z \rangle = 0 \end{aligned} \quad (5.15)$$

$$\begin{aligned} \langle p_y | \hat{L}_z | p_x \rangle &= i\hbar, & \langle p_x | \hat{L}_z | p_y \rangle &= -i\hbar, \\ \langle p_z | \hat{L}_x | p_y \rangle &= i\hbar, & \langle p_y | \hat{L}_x | p_z \rangle &= -i\hbar, \\ \langle p_x | \hat{L}_y | p_z \rangle &= i\hbar, & \langle p_z | \hat{L}_y | p_x \rangle &= -i\hbar. \end{aligned} \quad (5.16)$$

Note that

$$\begin{aligned} (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) |p_x\rangle &= -i\hbar \hat{L}_y |p_z\rangle + i\hbar \hat{L}_z |p_y\rangle = 2\hbar^2 |p_x\rangle \\ (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) |p_y\rangle &= 2\hbar^2 |p_y\rangle \\ (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) |p_z\rangle &= 2\hbar^2 |p_z\rangle \end{aligned} \quad (5.17)$$

The orbital angular momentum is zero (quenching of the orbital angular momentum).

B. Calculation of orbital angular momentum by Mathematica

Orbital angular momentum of 2p electron

$$L_z := \frac{\hbar}{i} (\mathbf{x} D[\#, \mathbf{y}] - \mathbf{y} D[\#, \mathbf{x}]) \&$$

$$L_x := \frac{\hbar}{i} (\mathbf{y} D[\#, \mathbf{z}] - \mathbf{z} D[\#, \mathbf{y}]) \&$$

$$L_y := \frac{\hbar}{i} (\mathbf{z} D[\#, \mathbf{x}] - \mathbf{x} D[\#, \mathbf{z}]) \&$$

$$\psi_x = \mathbf{x} f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right]; \quad \psi_y = \mathbf{y} f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right];$$

$$\psi_z = \mathbf{z} f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right];$$

$$\{L_z[\psi_x], L_z[\psi_y], L_z[\psi_z]\} // \text{Simplify}$$

$$\{i y \hbar f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right], -i x \hbar f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right], 0\}$$

$$\{L_x[\psi_x], L_x[\psi_y], L_x[\psi_z]\} // \text{Simplify}$$

$$\{0, i z \hbar f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right], -i y \hbar f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right]\}$$

$$\{L_y[\psi_x], L_y[\psi_y], L_y[\psi_z]\} // \text{Simplify}$$

$$\{-i z \hbar f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right], 0, i x \hbar f \left[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2} \right]\}$$

C. Theorem

If the state $|\psi\rangle$ is not degenerate, then the wave function $\langle \mathbf{r} | \psi \rangle$ should be real. Suppose that

$$\langle \mathbf{r} | \psi \rangle = \psi(\mathbf{r}) = f(\mathbf{r}) + ig(\mathbf{r}), \quad (5.18)$$

where f and g are real.

$$H\psi(\mathbf{r}) = H[f(\mathbf{r}) + ig(\mathbf{r})] = E[f(\mathbf{r}) + ig(\mathbf{r})], \quad (5.19)$$

or

$$\begin{aligned} Hf(\mathbf{r}) &= Ef(\mathbf{r}) \\ Hg(\mathbf{r}) &= Eg(\mathbf{r}) \end{aligned} \quad (5.20)$$

In other words, $f(\mathbf{r})$ and $g(\mathbf{r})$ are the eigenfunctions. This is inconsistent with the above assumption. Then $\psi(\mathbf{r})$ is real.

$$\psi^*(\mathbf{r}) = \psi(\mathbf{r}). \quad (5.21)$$

We consider the expectation

$$\langle \psi | \hat{\mathbf{L}} | \psi \rangle = \int d\mathbf{r} \langle \mathbf{r} | \psi \rangle^* \mathbf{L} \langle \mathbf{r} | \psi \rangle = \int d\mathbf{r} \psi^*(\mathbf{r}) \mathbf{L} \psi(\mathbf{r}). \quad (5.22)$$

$$\begin{aligned} \mathbf{L} &= \mathbf{r} \times \mathbf{p} = \frac{\hbar}{i} \mathbf{r} \times \nabla \\ \mathbf{L}^* &= -\frac{\hbar}{i} \mathbf{r} \times \nabla = -\mathbf{L} \end{aligned} \quad (5.23)$$

$$\langle \psi | \hat{\mathbf{L}} | \psi \rangle^* = \int d\mathbf{r} \psi(\mathbf{r}) \mathbf{L}^* \psi(\mathbf{r}) = -\int d\mathbf{r} [\psi(\mathbf{r}) \mathbf{L} \psi(\mathbf{r})] = -\langle \psi | \hat{\mathbf{L}} | \psi \rangle. \quad (5.24)$$

Since \mathbf{L} is a physical quantity (observable), we have

$$\langle \psi | \hat{\mathbf{L}} | \psi \rangle^* = \langle \psi | \hat{\mathbf{L}} | \psi \rangle. \quad (5.25)$$

Then we have

$$\langle \psi | \hat{\mathbf{L}} | \psi \rangle = 0 \quad (\text{the quenching of } \mathbf{L}). \quad (5.26)$$

For the orbital singlet

$$\langle \psi | \hat{\mathbf{L}} | \psi \rangle = 0. \quad (5.27)$$

5.4. Zeeman splitting of the orbital energy levels

The orbital magnetic moment is given by

$$\hat{\boldsymbol{\mu}}_L = -\mu_B \frac{\hat{\mathbf{L}}}{\hbar}. \quad (5.28)$$

The perturbation due to the Zeeman effect is described by

$$\hat{H}_{Zeeman} = -\hat{\boldsymbol{\mu}}_L \cdot \mathbf{H} = -(-\mu_B \frac{\hat{\mathbf{L}}}{\hbar}) \cdot \mathbf{H} = \frac{\mu_B H}{\hbar} \hat{L}_z. \quad (5.29)$$

The total perturbation is

$$\begin{aligned}
H' &= \hat{H}_{crystalfield} + \hat{H}_{Zeeman} \\
&= -A\hat{x}^2 - B\hat{y}^2 + (A+B)\hat{z}^2 + \frac{\mu_B H}{\hbar} \hat{L}_z
\end{aligned} \tag{5.30}$$

where the potential energy is defined by

$$\hat{H}_{crystalfield} = \hat{V} = -A\hat{x}^2 - B\hat{y}^2 + (A+B)\hat{z}^2$$

((Zeeman energy))

We assume that the new state is given by $|\psi\rangle$ with the energy eigenvalue E .

Eigenvalue problem

$$\begin{pmatrix}
\langle p_x | \hat{V} | p_x \rangle - E & \frac{\mu_B H}{\hbar} \langle p_x | \hat{L}_z | p_y \rangle & 0 \\
\frac{\mu_B H}{\hbar} \langle p_y | \hat{L}_z | p_x \rangle & \langle p_y | \hat{V} | p_y \rangle - E & 0 \\
0 & 0 & \langle p_z | \hat{V} | p_z \rangle - E
\end{pmatrix}
\begin{pmatrix}
\langle p_x | \psi \rangle \\
\langle p_y | \psi \rangle \\
\langle p_z | \psi \rangle
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
0
\end{pmatrix}, \tag{5.31}$$

or

$$\begin{pmatrix}
W_1 - E & -i\mu_B H & 0 \\
i\mu_B H & W_2 - E & 0 \\
0 & 0 & W_3 - E
\end{pmatrix}
\begin{pmatrix}
\langle p_x | \psi \rangle \\
\langle p_y | \psi \rangle \\
\langle p_z | \psi \rangle
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
0
\end{pmatrix}. \tag{5.32}$$

The eigenvalues are obtained as

$$W_3, \quad \frac{1}{2}[(W_1 + W_2) \pm \sqrt{(W_1 + W_2)^2 + 4\mu_B^2 H^2}]$$

5.5 Mathematica program: eigenvalue problem

We calculate the above eigenvalue problem using the Mathematica.

Effect of the crystal field on the energy level of the 2p electrons ($n = 2, l = 1$) wave functions

```

Clear["Global`*"];
rwave[n_, l_, r_] :=
  1
  /
  Sqrt[(n + l)!]
  (
    21+l a0-l-3/2 e-r/a0 n n-l-2 rl Sqrt[(n - l - 1)!]
    LaguerreL[-1 + n - l, 1 + 2 l, 2 r / a0 n]
  );

ψpx =
rwave[2, 1, r]
(
  -Sqrt[1/2] SphericalHarmonicY[1, 1, θ, φ] +
  Sqrt[1/2] SphericalHarmonicY[1, -1, θ, φ]
) //
FullSimplify[#, φ ∈ Reals] &;

ψpy =
rwave[2, 1, r]
(
  i Sqrt[1/2] (SphericalHarmonicY[1, 1, θ, φ] +
  SphericalHarmonicY[1, -1, θ, φ])
) // FullSimplify[#, φ ∈ Reals] &;

ψpz = rwave[2, 1, r] SphericalHarmonicY[1, 0, θ, φ] // Simplify;
rule1 = {x → r Sin[θ] Cos[φ], y → r Sin[θ] Sin[φ], z → r Cos[θ]};
V = -A x2 - B y2 + (A + B) z2 /. rule1 // Simplify;

J[1, 1] = ψpx V ψpx; J[1, 2] = ψpx V ψpy; J[1, 3] = ψpx V ψpz;
J[2, 1] = ψpy V ψpx; J[2, 2] = ψpy V ψpy; J[2, 3] = ψpy V ψpz;
J[3, 1] = ψpz V ψpx; J[3, 2] = ψpz V ψpy;
J[3, 3] = ψpz V ψpz;

H1[p_, q_] :=
Integrate[Integrate[Integrate[2 π r2 Sin[θ] J[p, q], {φ, 0, 2 π}],
{θ, 0, π}], {r, 0, ∞}] // Simplify[#, Re[a0] > 0] &

H12 = Table[H1[p, q], {p, 1, 3}, {q, 1, 3}]
{{-24 A a02 π, 0, 0}, {0, -24 a02 B π, 0}, {0, 0, 24 a02 (A + B) π}}

H12 // TableForm
-24 A a02 π    0          0
0              -24 a02 B π  0
0              0          24 a02 (A + B) π

H13 = Eigensystem[H12]
{{-24 A a02 π, -24 a02 B π, 24 a02 (A + B) π},
{{1, 0, 0}, {0, 1, 0}, {0, 0, 1}}

```

```

E1 = H13[[1, 2]]; E2 = H13[[1, 1]]; E3 = H13[[1, 3]];

{E1, E2, E3} /. {A -> 2, B -> 1} // N
{-75.3982 a0^2, -150.796 a0^2, 226.195 a0^2}

```

Zeeman effect

We consider the eigen value problem

$$A = \{W_1, -i \mu_B H, 0\}, \{i \mu_B H, W_2, 0\}, \{0, 0, W_3\}$$

```

HH = {{W1, -i \mu_B H, 0}, {i \mu_B H, W2, 0}, {0, 0, W3}}
{{W1, -i H \mu_B, 0}, {i H \mu_B, W2, 0}, {0, 0, W3}}

```

```
HH // MatrixForm
```

$$\begin{pmatrix} W_1 & -i H \mu_B & 0 \\ i H \mu_B & W_2 & 0 \\ 0 & 0 & W_3 \end{pmatrix}$$

```
eq1 = Eigenvalues[HH]
```

$$\left\{ W_3, \frac{1}{2} \left(W_1 + W_2 - \sqrt{W_1^2 - 2 W_1 W_2 + W_2^2 + 4 H^2 \mu_B^2} \right), \frac{1}{2} \left(W_1 + W_2 + \sqrt{W_1^2 - 2 W_1 W_2 + W_2^2 + 4 H^2 \mu_B^2} \right) \right\}$$

```
rule2 = {W1 -> E1, W2 -> E2, W3 -> E3};
```

```
rule3 = {\mu_B -> 1, A -> 2, B -> 1, a0 -> 1};
```

```
W11 = eq1[[2]] /. rule2 /. rule3 // N;
```

```
W22 = eq1[[3]] /. rule2 /. rule3 // N;
```

```
W33 = eq1[[1]] /. rule2 /. rule3 // N;
```

```

Plot[Evaluate[{W11, W22, W33} /. a0 -> 1], {H, 0, 100},
PlotStyle -> {{Hue[0], Thick}, {Hue[0.4], Thick}, {Hue[0.8], Thick}},
Prolog -> AbsoluteThickness[1.5], PlotPoints -> 100,
Background -> GrayLevel[0.7], AxesLabel -> {"H", "Energy"}]

```

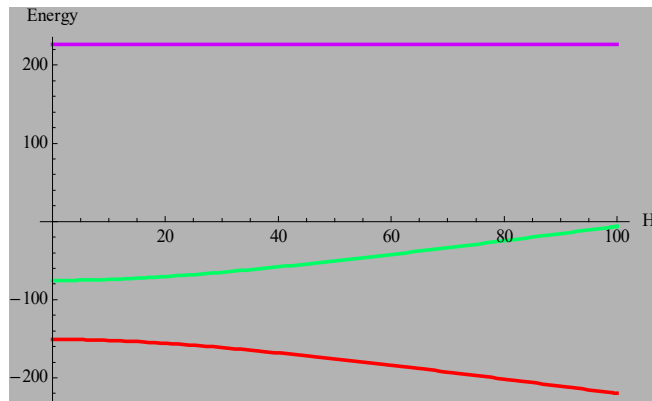


Fig.10

Zeeman splitting of the energy level W_1 and W_2 . We assume that $a_0 = 1$, $\mu_B = 1$, $A = 2$ and $B = 1$.

6. 3d-electrons in the crystal field

6.1. 3d-electron wave functions

We now consider the origin of the splitting of the orbital levels by the crystal field. Suppose that an ion with only one 3d electron ($n = 3$ and $l = 2$). It forms wave functions made up of certain combinations of the 3d hydrogen wave functions. The linear combinations we choose are

$$\begin{aligned}
 \psi_{xy} &= -i \frac{1}{\sqrt{2}} [Y_2^2(\theta, \phi) - Y_2^{-2}(\theta, \phi)] \\
 \psi_{yz} &= i \frac{1}{\sqrt{2}} [Y_2^1(\theta, \phi) + Y_2^{-1}(\theta, \phi)] \\
 \psi_{zx} &= -\frac{1}{\sqrt{2}} [Y_2^1(\theta, \phi) - Y_2^{-1}(\theta, \phi)] \quad , \\
 \psi_{x^2-y^2} &= \frac{1}{\sqrt{2}} [Y_2^2(\theta, \phi) + Y_2^{-2}(\theta, \phi)] \\
 \psi_{3z^2-r^2} &= Y_2^0(\theta, \phi)
 \end{aligned} \tag{6.1}$$

or

$$\begin{aligned}
 |\psi_1\rangle &= |\psi_{xy}\rangle = -i \frac{1}{\sqrt{2}} [|l=2, m=2\rangle - |l=2, m=-2\rangle] \\
 |\psi_2\rangle &= |\psi_{yz}\rangle = i \frac{1}{\sqrt{2}} [|2, 1\rangle + |2, -1\rangle] \\
 |\psi_3\rangle &= |\psi_{zx}\rangle = -\frac{1}{\sqrt{2}} [|2, 1\rangle - |2, -1\rangle] \quad . \\
 |\psi_4\rangle &= |\psi_{x^2-y^2}\rangle = \frac{1}{\sqrt{2}} [|2, 2\rangle + |2, -2\rangle] \\
 |\psi_5\rangle &= |\psi_{3z^2-r^2}\rangle = |2, 0\rangle
 \end{aligned} \tag{6.2}$$

Note that the notation of the spherical harmonics used here is the same as that used in the Mathematica.

((**Mathematica**)) Spherical harmonics $Y_l^m(\theta, \phi)$

```

Clear["Global`*"];
Table[{2, m, SphericalHarmonicY[2, m,  $\theta$ ,  $\phi$ ]},
      {m, -2, 2, 1}] // TableForm

```

$$\begin{array}{ccc}
2 & -2 & \frac{1}{4} e^{-2i\phi} \sqrt{\frac{15}{2\pi}} \sin^2[\theta] \\
2 & -1 & \frac{1}{2} e^{-i\phi} \sqrt{\frac{15}{2\pi}} \cos[\theta] \sin[\theta] \\
2 & 0 & \frac{1}{4} \sqrt{\frac{5}{\pi}} (-1 + 3 \cos^2[\theta]) \\
2 & 1 & -\frac{1}{2} e^{i\phi} \sqrt{\frac{15}{2\pi}} \cos[\theta] \sin[\theta] \\
2 & 2 & \frac{1}{4} e^{2i\phi} \sqrt{\frac{15}{2\pi}} \sin^2[\theta]
\end{array}$$

Table 1 Spherical harmonics $\{l, m, Y_l^m(\theta, \phi)\}$. $l = 2$. $m = 2, 1, 0, -1, -2$.

The radial part of the wave function ($n = 3$ and $l = 2$) is given by

$$R_{3,2}(r) = 2\sqrt{\frac{2}{15}} \frac{1}{81a_0^{7/2}} r^2 \exp\left(-\frac{r}{3a_0}\right). \quad (6.3)$$

There are two types of orbital states: the $d\varepsilon$ orbitals d_{xy} , d_{yz} , d_{zx} , the $d\gamma$ orbitals: $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. The complete wavefunctions are given as follows.

$d\varepsilon(t_{2g})$

$$\begin{aligned}
\langle \mathbf{r} | d_{xy} \rangle &= \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{2xy}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}} \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \sqrt{3}xy \\
\langle \mathbf{r} | d_{yz} \rangle &= \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{2yz}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}} \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \sqrt{3}yz, \\
\langle \mathbf{r} | d_{zx} \rangle &= \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{2zx}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}} \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \sqrt{3}zx
\end{aligned} \quad (6.4a)$$

$d\gamma(e_g)$

$$\begin{aligned} \langle \mathbf{r} | d_{x^2-y^2} \rangle &= \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{x^2-y^2}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}} \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{\sqrt{3}(x^2-y^2)}{2} \\ \langle \mathbf{r} | d_{3z^2-r^2} \rangle &= \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{3z^2-r^2}{\sqrt{6\pi}} = \frac{2}{\sqrt{6\pi}} \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{3z^2-r^2}{2} \end{aligned} \quad (6.4b)$$

For convenience, we use the notations: $\langle \mathbf{r} | d_{xy} \rangle = \psi_1$, $\langle \mathbf{r} | d_{yz} \rangle = \psi_2$, $\langle \mathbf{r} | d_{zx} \rangle = \psi_3$, $\langle \mathbf{r} | d_{x^2-y^2} \rangle = \psi_4$, $\langle \mathbf{r} | d_{3z^2-r^2} \rangle = \psi_5$. The complete wavefunctions are given by

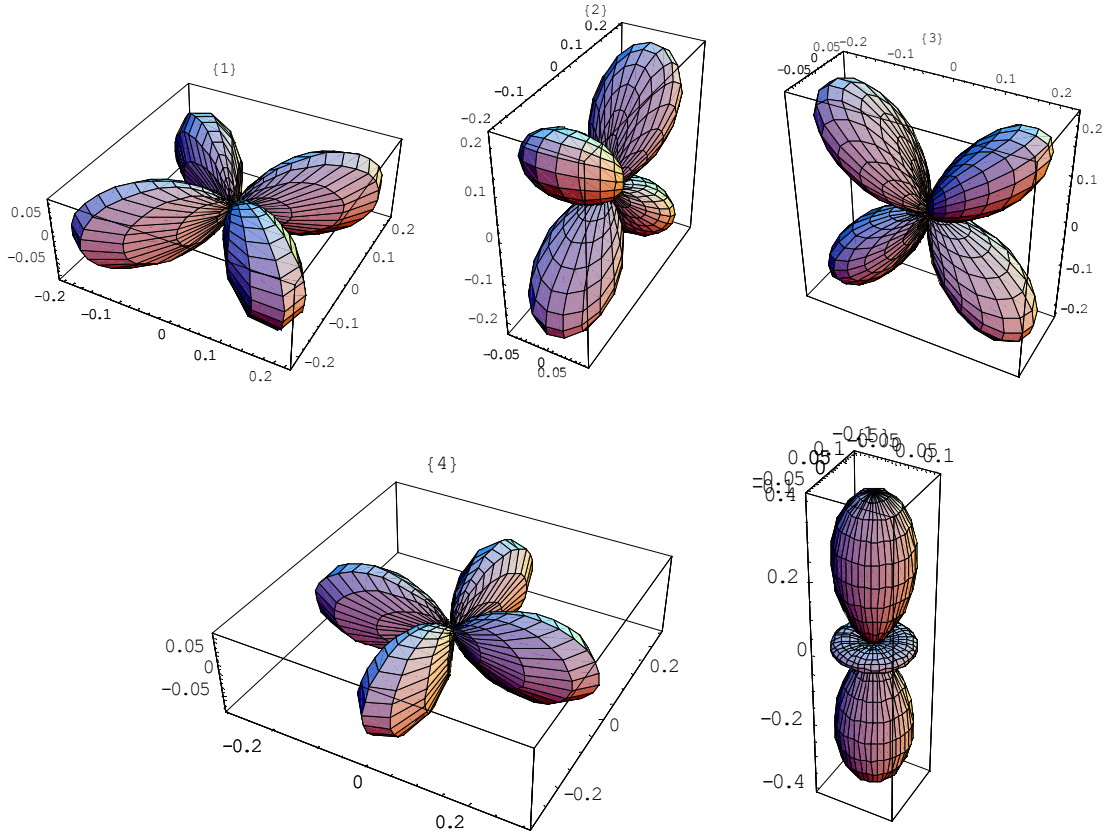


Fig.11 Angular parts of the wavefunctions for (1) d_{xy} , (2) d_{yz} , (3) d_{zx} , (4) $d_{x^2-y^2}$, and (5) $d_{3z^2-r^2}$.

6.2. Orthorhombic crystal field

We consider the octahedral field (cubic). There are 6 negative ions around one 3d electron at (0,0,0). The negative ions are located at $(\pm a, 0, 0)$, $(0, \pm a, 0)$, and $(0, 0, \pm a)$. The Coulomb repulsion energy (positive) is large for the $d\gamma$ orbitals [for example, $d_{x^2-y^2}$].

Suppose that six negative ions X with charge $-e$ are located on the x -, y -, and z - axes at a distance a from the origin. When $r < a$, the electrostatic potential energy due to the ligand field is given by

$$V(r) = V_0 + D(x^4 + y^4 + z^4 - \frac{3}{5}r^4). \quad (6.5)$$

with

$$V_0 = \frac{6Ze^2}{a} \quad \text{and} \quad D = \frac{35Ze^2}{4a^5}$$

This is an explicit expression for the cubic ligand field in the point charge approximation. The symmetry of the Hamiltonian for the 3d electron is now lowered from spherical to cubic because of the presence of the ligand field.

The electron charge cloud distributions of the orbitals are sketched in Fig.7. It is easier for a 3d electron cloud to avoid the charge cloud of the neighboring negative ions. The orbitals ($d\varepsilon$) will then have a lower energy than for the orbitals ($d\gamma$).

(i) Charge distribution of d_{xy} in the x - y plane

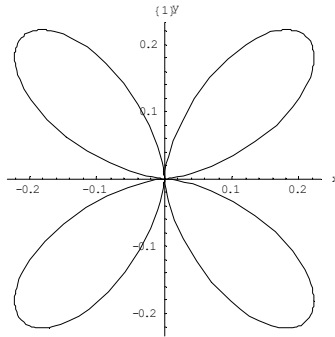


Fig.12(a) Representation of d_{xy} orbit in the x - y plane.

The Coulomb repulsion energy is *small* for the d_{xy} because of the existence of the neighboring negative charges located at $(\pm a, 0, 0)$ and $(0, \pm a, 0)$.

(ii) Charge distribution of $d(yz)$ in the y - z plane

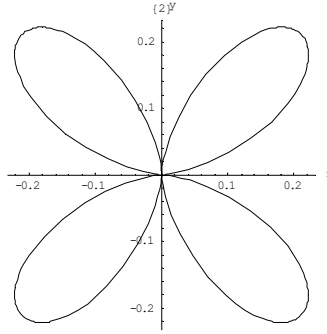


Fig.12(b) Representation of d_{yz} orbit in the y - z plane.

The Coulomb repulsion energy is *small* for the d_{yz} because of the existence of the neighboring negative charges located at $(0, \pm a, 0)$ and $(0, 0, \pm a)$.

(iii) Charge distribution for d_{zx} in the z - x plane

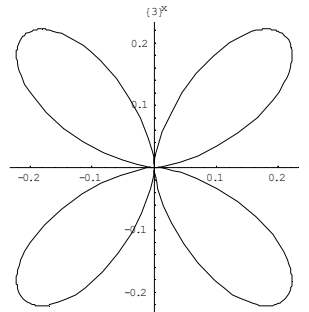


Fig.12(c) Representation of d_{zx} orbit in the x - z plane.

The Coulomb repulsion energy is *small* for the d_{zx} because of the existence of the neighboring negative charges located at $(0, 0, \pm a, 0)$ and $(\pm a, 0, 0)$.

(iv) Charge distribution of $d_{x^2-y^2}$ in the x - y plane

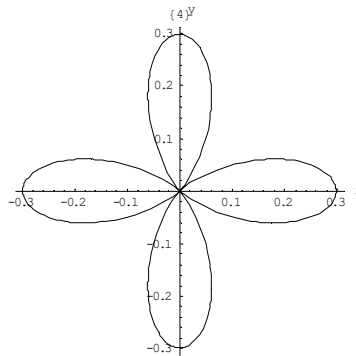


Fig.12(d) Representation of $d_{x^2-y^2}$ orbit in the x - y plane.

The Coulomb repulsion energy is *large* for the $d_{x^2-y^2}$ because of the existence of the neighboring negative charges located at $(\pm a, 0, 0)$ and $(0, \pm a, 0)$.

(v) Charge distribution of $d_{3z^2-r^2}$ in the z - x plane

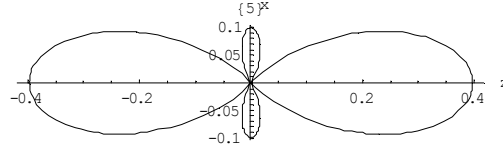


Fig.12(e) Representation of $d_{3z^2-r^2}$ orbit in the z - x plane.

The Coulomb repulsion energy is large for the $d_{3z^2-r^2}$, because of the existence of the neighboring negative charges located at $(0,0,\pm a)$.

6.3. Wave function of $(3d)^1$ electron in the orthorhombic field

Matrix element is defined by

$$\langle i|\hat{V}|j\rangle = \int \langle \mathbf{r}|d(i)\rangle^* V(\mathbf{r}) \langle \mathbf{r}|d(j)\rangle \quad (6.6)$$

$$\begin{pmatrix} -4Dq & 0 & 0 & 0 & 0 \\ 0 & -4Dq & 0 & 0 & 0 \\ 0 & 0 & -4Dq & 0 & 0 \\ 0 & 0 & 0 & 6Dq & 0 \\ 0 & 0 & 0 & 0 & 6Dq \end{pmatrix}. \quad (6.7)$$

We have eigenvalues and eigenfunctions

$$E = -4Dq \text{ for } |d_{xy}\rangle, |d_{yz}\rangle, |d_{zx}\rangle, \quad (6.8)$$

and

$$E = 6Dq \text{ for } |d_{x^2-y^2}\rangle, |d_{3z^2-r^2}\rangle. \quad (6.9)$$

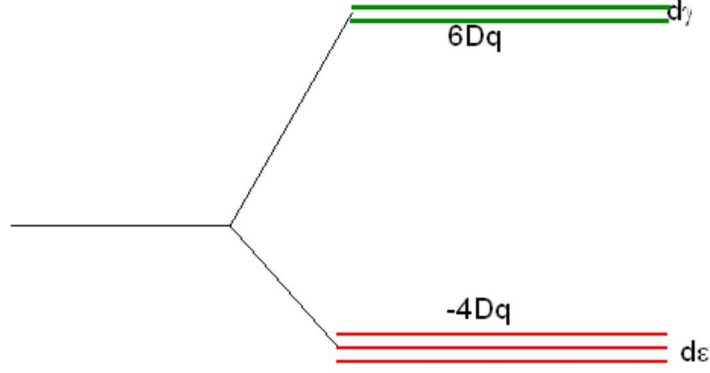


Fig.13 Splitting of the energy level (2D) of ground state of free $(3d)^1$ under the octahedral field.

where the energy difference between two levels is called $10 Dq$,

$$q = \frac{2}{105} \langle r^4 \rangle = 486a_0^4, \quad (6.10)$$

$$\langle r^4 \rangle = \int_0^{\infty} r^4 r^2 dr |R_{32}(r)|^2 = 2.5515 \times 10^4 a_0^4. \quad (6.11)$$

((Note))

We have some comment on the independence of the $d\gamma$ -orbital wave function (there are only two independent states).

$$\langle \mathbf{r} | d_{x^2-y^2} \rangle = \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{x^2 - y^2}{\sqrt{2\pi}} \quad (6.12)$$

$$\langle \mathbf{r} | d_{3z^2-r^2} \rangle = \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{3z^2 - r^2}{\sqrt{6\pi}} = \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{3z^2 - (x^2 + y^2 + z^2)}{\sqrt{6\pi}} \quad (6.13)$$

or

$$\begin{aligned} \langle \mathbf{r} | d_{3z^2-r^2} \rangle &= \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{2z^2 - (x^2 + y^2)}{\sqrt{6\pi}} \\ &= \frac{1}{81a_0^{7/2}} \exp\left(-\frac{r}{3a_0}\right) \frac{(z^2 - x^2) + (z^2 - y^2)}{\sqrt{6\pi}}. \end{aligned} \quad (6.14)$$

There are two independent states since

$$\langle \mathbf{r} | d_{x^2-y^2} \rangle + \langle \mathbf{r} | d_{y^2-z^2} \rangle + \langle \mathbf{r} | d_{z^2-x^2} \rangle = 0, \quad (6.15)$$

$$\langle \mathbf{r} | d_{3z^2-r^2} \rangle = \frac{\langle \mathbf{r} | d_{z^2-x^2} \rangle - \langle \mathbf{r} | d_{y^2-z^2} \rangle}{\sqrt{3}}. \quad (6.16)$$

6.4. Wave function of $(3d)^1$ electron in the tetragonal field

A. Eigenvalue problem

We now consider the case where $a = b \neq c$. The static potential energy is given by

$$\begin{aligned} V(\mathbf{r}) = Ze^2 \left[\frac{4}{a} + \frac{2}{c} + A(x^2 + y^2 - 2z^2) + D(x^4 + y^4 + z^4) \right. \\ \left. + Q(z^4 + 6x^2y^2) - \frac{3}{4} \left(\frac{3}{a^5} + \frac{4}{c^5} \right) r^4 \right]. \end{aligned} \quad (6.17)$$

where

$$\begin{aligned} A = \left(\frac{1}{a^3} - \frac{1}{c^3} \right), \quad D = \frac{5}{4} \left(\frac{4}{a^5} + \frac{3}{c^5} \right) > 0, \\ Q = -\frac{5}{4} \left(\frac{1}{a^5} - \frac{1}{c^5} \right), \quad \varepsilon = \frac{3}{4} \left(\frac{3}{a^5} + \frac{4}{c^5} \right) > 0. \end{aligned} \quad (6.18)$$

The sign of A and Q changes depending on the ratio of c/a . On the other hand, D and ε are always positive. Here the matrix element is defined by

$$\langle i | \hat{V} | j \rangle = \int \langle \mathbf{r} | d(i) \rangle^* V(\mathbf{r}) \langle \mathbf{r} | d(j) \rangle = \begin{pmatrix} W_{11} & 0 & 0 & 0 & 0 \\ 0 & W_{22} & 0 & 0 & 0 \\ 0 & 0 & W_{33} & 0 & 0 \\ 0 & 0 & 0 & W_{44} & 0 \\ 0 & 0 & 0 & 0 & W_{55} \end{pmatrix}. \quad (6.19)$$

$$W_{11} = \frac{Ze^2}{ca} [4c + a(2 + 72ca_0^2 A + 1215ca_0^4 (11D + 19Q - 21\varepsilon))]$$

$$W_{22} = \frac{Ze^2}{ca} [4c + a(2 + 9ca_0^2 (-4A + 135a_0^2 (11(D + Q) - 21\varepsilon)))]$$

$$W_{33} = \frac{Ze^2}{ca} [4c + a(2 + 9ca_0^2 (-4A + 135a_0^2 (11(D + Q) - 21\varepsilon)))]$$

$$W_{44} = \frac{Ze^2}{ca} [4c + a(2 + 72ca_0^2 A + 1215ca_0^4 (15D + 7Q - 21\varepsilon))]$$

$$W_{55} = \frac{Ze^2}{ca} [4c + a(2 + 9ca_0^2 (-8A + 405a_0^2 (5(D + Q) - 7\varepsilon)))]$$

Here we use the perturbation theory (degenerate case) (see the Mathematica program below).

B. Eigenvalue problem

The eigenvalues

$$\begin{aligned} E_1 &= W_{11} \text{ for } d_{xy}, \\ E_2 &= W_{22} \text{ for } d_{yz}, \\ E_3 &= W_{33} \text{ for } d_{zx}, \\ E_4 &= W_{44} \text{ for } d_{x^2-y^2}, \end{aligned}$$

and

$$E_5 = W_{55} \text{ for } d_{3z^2-r^2}.$$

We note that

$$\begin{aligned} E_4 &= E_5 = E_1 + 10Dq, \\ E_1 &= E_2 = E_3 \end{aligned}$$

in the limit of $A \rightarrow 0$, $Q \rightarrow 0$, and $\varepsilon \rightarrow 0$. In the general case,

$$\begin{aligned} \frac{E_4 - E_1}{Dq} &= 10 - \frac{30Q}{D} & \frac{E_5 - E_1}{Dq} &= 10 - \frac{8A}{27a_0^2 D} - \frac{10Q}{D} \\ \frac{E_3 - E_1}{Dq} &= -\frac{2A}{9a_0^2 D} - \frac{20Q}{D} & \frac{E_3 - E_2}{Dq} &= 0 \text{ (} E_2 \text{ and } E_3 \text{ are degenerate).} \\ \frac{E_5 - E_4}{Dq} &= -\frac{8A}{27a_0^2 D} + \frac{20Q}{D} \end{aligned}$$

We now make a plot of the energy levels (normalized by Dq) as a function of c/a_0 , where a/a_0 is fixed as a parameter and a_0 is the Bohr radius. For convenience we choose $a/a_0 = 10$ ($a = 10 a_0 = 5.3 \text{ \AA}$).

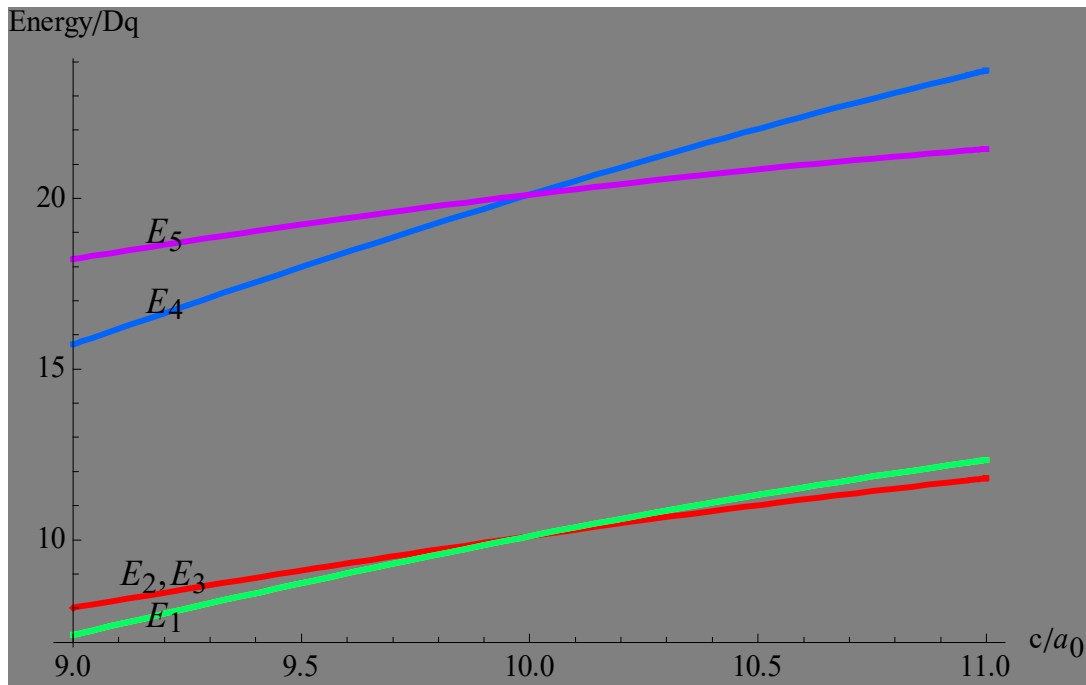


Fig.14 Energy levels for the tetragonal case, as a function of c/a_0 . $a/a_0 = 10$. [d_{xy} (green), d_{yz} (red), d_{zx} (red), $d_{x^2-y^2}$ (blue), and $d_{3z^2-r^2}$ (purple)]. The energy level of d_{yz} and d_{zx} (degenerate) is higher than that of d_{xy} for $c < a$, while the energy level of d_{yz} and d_{zx} (degenerate) is lower than that of d_{xy} for $c > a$. The energy level of $d_{3z^2-r^2}$ is higher than that of $d_{x^2-y^2}$ for $c < a$, while the energy level of $d_{3z^2-r^2}$ is lower than that of $d_{x^2-y^2}$ for $c > a$.

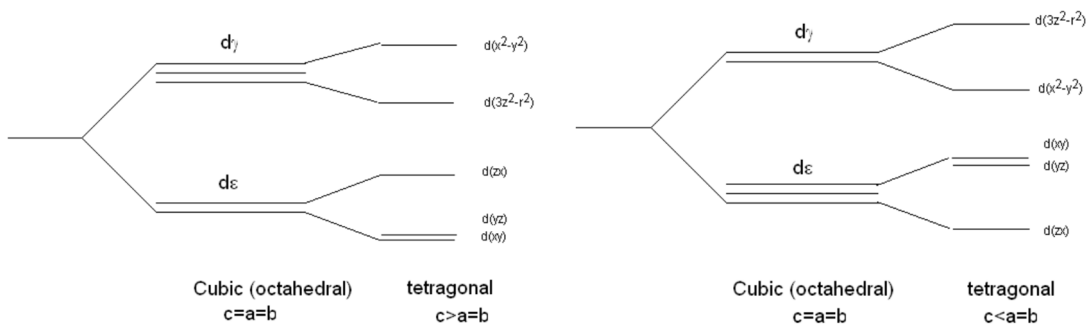


Fig.15 Energy diagram for $(3d)^1$ ion in the octahedral and tetragonal cases for (i) $c > a = b$. (ii) $c < a = b$.

C. Mathematica program: Eigenvalue problem

Using the Mathematica program we solve the eigenvalue problems. The result obtained is shown in Fig.14.

Wavefunctions for one 3d electron in the tetragonal case

```
Clear["Global`"];
Needs["VectorAnalysis`"];
SetCoordinates[Cartesian[x, y, z]];
V =
  z e0^2 ( 4/a + 2/c + A1 (x^2 + y^2 - 2 z^2) + D1 (x^4 + y^4 + z^4) +
    Q1 (z^4 + 6 x^2 y^2) - e1 (x^2 + y^2 + z^2)^2 );
rule1 = {A1 -> (1/a^3 - 1/c^3), D1 -> (20/(4 a^5) + 15/(4 c^5)), Q1 -> -(5/(4 a^5) - 5/(4 c^5)),
  e1 -> (9/(4 a^5) + 12/(4 c^5))};
rule2 = {x -> r Sin[theta] Cos[phi], y -> r Sin[theta] Sin[phi], z -> r Cos[theta]};
V1 = V /. rule2 // TrigFactor;
```

wave functions of d-orbitals

$$\psi[1] = \frac{e^{-\frac{r}{3a_0}} r^2 \sin[\theta]^2 \sin[2\phi]}{81 a_0^{7/2} \sqrt{2\pi}} ;$$

$$\psi[2] = \frac{e^{-\frac{r}{3a_0}} r^2 \sin[2\theta] \sin[\phi]}{81 a_0^{7/2} \sqrt{2\pi}} ; \psi[3] = \frac{e^{-\frac{r}{3a_0}} r^2 \cos[\phi] \sin[2\theta]}{81 a_0^{7/2} \sqrt{2\pi}} ;$$

$$\psi[4] = \frac{e^{-\frac{r}{3a_0}} r^2 \cos[2\phi] \sin[\theta]^2}{81 a_0^{7/2} \sqrt{2\pi}} ;$$

$$\psi[5] = \frac{e^{-\frac{r}{3a_0}} r^2 (1 + 3 \cos[2\theta])}{162 a_0^{7/2} \sqrt{6\pi}}$$

$$\frac{e^{-\frac{r}{3a_0}} r^2 (1 + 3 \cos[2\theta])}{162 a_0^{7/2} \sqrt{6\pi}}$$

Rnl(r): radial part of wave function; n = 3, l = 2.

$$\text{rwave}[3, 2, r] = \frac{2 \sqrt{\frac{2}{15}} e^{-\frac{r}{3a_0}} r^2}{81 a_0^{7/2}} ;$$

Average of r^4

```
r4av = Integrate[ r^4 r^2 rwave[3, 2, r]^2, {r, 0, ∞}] //  
FullSimplify[#, Re[a0] > 0] &  
25515 a0^4
```

$$q1 = \frac{2}{105} \langle r^4 \rangle$$

```
q4 =  $\frac{2}{105}$  r4av // Simplify  
486 a0^4
```

Average of r^2

```
r2av = Integrate[ r^2 r^2 rwave[3, 2, r]^2, {r, 0, ∞}] //  
FullSimplify[#, Re[a0] > 0] &  
126 a0^2
```

Matrix element calculations

```
J[p_, q_] :=  $\psi[p]$  v1  $\psi[q]$ ;
```

```
Norm1[p_, q_] :=  $\psi[p]$   $\psi[q]$ 
```

Average of r^4

```
r4av = Integrate[ r^4 r^2 rwave[3, 2, r]^2, {r, 0, ∞}] //  
FullSimplify[#, Re[a0] > 0] &  
25515 a0^4
```

$$q1 = \frac{2}{105} \langle r^4 \rangle$$

```
q4 =  $\frac{2}{105}$  r4av // Simplify  
486 a0^4
```

Average of r^2

```
r2av = Integrate[ r^2 r^2 rwave[3, 2, r]^2, {r, 0, ∞}] //  
FullSimplify[#, Re[a0] > 0] &  
126 a0^2
```

Matrix element calculations

```
J[p_, q_] :=  $\psi[p]$  v1  $\psi[q]$ ;
```

```
Norm1[p_, q_] :=  $\psi[p]$   $\psi[q]$ 
```

$$\left\{ 10 - \frac{30 Q_1}{D_1}, 10 - \frac{8 A_1}{27 a_0^2 D_1} - \frac{10 Q_1}{D_1}, \right. \\ \left. - \frac{2 A_1}{9 a_0^2 D_1} - \frac{20 Q_1}{D_1}, 0, - \frac{8 A_1}{27 a_0^2 D_1} + \frac{20 Q_1}{D_1} \right\}$$

`rule3 = {a → a0 α, c → a0 β};`

$$E_{50} = \frac{E_5}{D_0 q^4} /. rule1 /. rule3 // Simplify;$$

$$E_{40} = \frac{E_4}{D_0 q^4} /. rule1 /. rule3 // Simplify;$$

$$E_{30} = \frac{E_3}{D_0 q^4} /. rule1 /. rule3 // Simplify;$$

$$E_{20} = \frac{E_2}{D_0 q^4} /. rule1 /. rule3 // Simplify;$$

$$E_{10} = \frac{E_1}{D_0 q^4} /. rule1 /. rule3 // Simplify;$$

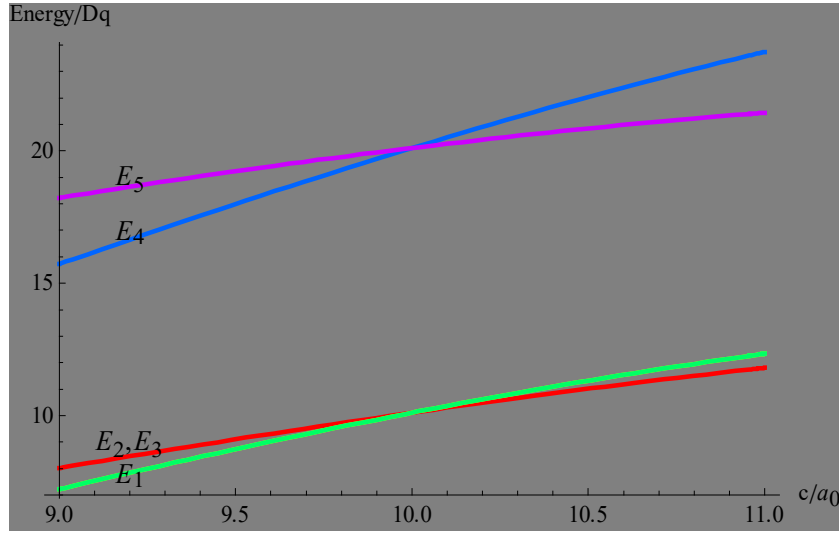
`Energy = {E10, E20, E30, E40, E50};`

Energy diagram

```

f1 = Plot[Evaluate[Energy /.  $\alpha \rightarrow 10$ ], { $\beta$ , 9, 11},
  PlotStyle  $\rightarrow$  Table[{Thick, Hue[0.2 i]}, {i, 0, 5}],
  Background  $\rightarrow$  GrayLevel[0.5],
  AxesLabel  $\rightarrow$  {"c/a0", "Energy/Dq"}];
f2 = Graphics[{Text[Style["E1", Black, 12], {9.2, 7.8}],
  Text[Style["E2, E3", Black, 12], {9.2, 9}],
  Text[Style["E4", Black, 12], {9.2, 17}],
  Text[Style["E5", Black, 12], {9.2, 19}]]];
Show[f1, f2]

```



D. Quenching of orbital angular momentum

For the orbital singlet, the average of the orbital angular momentum is equal to zero.

$$\begin{aligned}
\hat{L}_z|\psi_1\rangle &= -2i\hbar|\psi_4\rangle & \hat{L}_x|\psi_1\rangle &= i\hbar|\psi_3\rangle & \hat{L}_y|\psi_1\rangle &= -i\hbar|\psi_2\rangle \\
\hat{L}_z|\psi_2\rangle &= -i\hbar|\psi_3\rangle & \hat{L}_x|\psi_2\rangle &= i\hbar[|\psi_4\rangle + \sqrt{3}|\psi_5\rangle] & \hat{L}_y|\psi_2\rangle &= i\hbar|\psi_1\rangle \\
\hat{L}_z|\psi_3\rangle &= i\hbar|\psi_2\rangle & \hat{L}_x|\psi_3\rangle &= -i\hbar|\psi_1\rangle & \hat{L}_y|\psi_3\rangle &= i\hbar(|\psi_4\rangle - \sqrt{3}|\psi_5\rangle), \\
\hat{L}_z|\psi_4\rangle &= 2i\hbar|\psi_1\rangle & \hat{L}_x|\psi_4\rangle &= -i\hbar|\psi_2\rangle & \hat{L}_y|\psi_4\rangle &= -i\hbar|\psi_3\rangle \\
\hat{L}_z|\psi_5\rangle &= 0 & \hat{L}_x|\psi_5\rangle &= -i\sqrt{3}\hbar|\psi_2\rangle & \hat{L}_y|\psi_5\rangle &= i\hbar\sqrt{3}|\psi_3\rangle
\end{aligned}
\tag{6.20}$$

$$\begin{aligned}
\hat{L}_+|\psi_1\rangle &= |\psi_2\rangle + i|\psi_3\rangle & \hat{L}_-|\psi_1\rangle &= -|\psi_2\rangle + i|\psi_3\rangle \\
\hat{L}_+|\psi_2\rangle &= -|\psi_1\rangle + i|\psi_4\rangle + i\sqrt{3}|\psi_5\rangle & \hat{L}_-|\psi_2\rangle &= |\psi_1\rangle + i|\psi_4\rangle + i\sqrt{3}|\psi_5\rangle \\
\hat{L}_+|\psi_3\rangle &= -i|\psi_1\rangle - |\psi_4\rangle + \sqrt{3}|\psi_5\rangle, & \hat{L}_-|\psi_3\rangle &= -i|\psi_1\rangle + |\psi_4\rangle - \sqrt{3}|\psi_5\rangle. \quad (6.21) \\
\hat{L}_+|\psi_4\rangle &= -i|\psi_2\rangle + |\psi_3\rangle & \hat{L}_-|\psi_4\rangle &= -i|\psi_2\rangle - |\psi_3\rangle \\
\hat{L}_+|\psi_5\rangle &= -i\sqrt{3}|\psi_2\rangle - \sqrt{3}|\psi_3\rangle & \hat{L}_-|\psi_5\rangle &= -i\sqrt{3}|\psi_2\rangle + \sqrt{3}|\psi_3\rangle
\end{aligned}$$

$$\begin{aligned}
\langle\psi_i|\hat{L}_z|\psi_i\rangle &= 0 \\
\langle\psi_i|\hat{L}_x|\psi_i\rangle &= 0, \quad (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)|\psi_i\rangle = 6\hbar^2|\psi_i\rangle, \quad (i = 1 - 5). \quad (6.22) \\
\langle\psi_i|\hat{L}_y|\psi_i\rangle &= 0
\end{aligned}$$

E. Mathematica program

Using the Mathematica we show the formula of the orbital angular momentum in quantum mechanics.

((Mathematica-1))

Orbital angular momentum of 3d electron

```

Clear["Global`*"];

Lz :=  $\frac{\hbar}{i} (\mathbf{x} \cdot \mathbf{D}[\#, \mathbf{y}] - \mathbf{y} \cdot \mathbf{D}[\#, \mathbf{x}]) \ \&$ ;

Lx :=  $\frac{\hbar}{i} (\mathbf{y} \cdot \mathbf{D}[\#, \mathbf{z}] - \mathbf{z} \cdot \mathbf{D}[\#, \mathbf{y}]) \ \&$ ;

Ly :=  $\frac{\hbar}{i} (\mathbf{z} \cdot \mathbf{D}[\#, \mathbf{x}] - \mathbf{x} \cdot \mathbf{D}[\#, \mathbf{z}]) \ \&$ ;

 $\psi_1 = \sqrt{3} \ \mathbf{x} \ \mathbf{y} \ f[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2}]$ ;  $\psi_2 = \sqrt{3} \ \mathbf{y} \ \mathbf{z} \ f[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2}]$ ;

 $\psi_3 = \sqrt{3} \ \mathbf{z} \ \mathbf{x} \ f[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2}]$ ;

 $\psi_4 = \frac{\sqrt{3}}{2} (\mathbf{x}^2 - \mathbf{y}^2) \ f[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2}]$ ;

 $\psi_5 = \frac{1}{2} (3 \ \mathbf{z}^2 - (\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2)) \ f[\sqrt{\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2}]$ ;

{Lz[ψ1], Lz[ψ2], Lz[ψ3], Lz[ψ4], Lz[ψ5]} // Simplify

{-i √3 (x² - y²) ħ f[√(x² + y² + z²)],
 -i √3 x z ħ f[√(x² + y² + z²)], i √3 y z ħ f[√(x² + y² + z²)],
 2 i √3 x y ħ f[√(x² + y² + z²)], 0}

{Lx[ψ1], Lx[ψ2], Lx[ψ3], Lx[ψ4], Lx[ψ5]} // Simplify

{i √3 x z ħ f[√(x² + y² + z²)], -i √3 (y² - z²) ħ f[√(x² + y² + z²)],
 -i √3 x y ħ f[√(x² + y² + z²)],
 -i √3 y z ħ f[√(x² + y² + z²)], -3 i y z ħ f[√(x² + y² + z²)]}

{Ly[ψ1], Ly[ψ2], Ly[ψ3], Ly[ψ4], Ly[ψ5]} // Simplify

{-i √3 y z ħ f[√(x² + y² + z²)],
 i √3 x y ħ f[√(x² + y² + z²)], i √3 (x² - z²) ħ f[√(x² + y² + z²)],
 -i √3 x z ħ f[√(x² + y² + z²)], 3 i x z ħ f[√(x² + y² + z²)]}

```

((Mathematica-2))

L = 2 matrix element in quantum mechanics

```
conjugateRule = {Complex [re_ , im_] :=> Complex [re , -im]};  
Unprotect [SuperStar ];  
SuperStar /: exp_ * := exp /. conjugateRule ;
```

Matrix element of orbital angular momentum L = 2

```
Jx[l_, n_, m_] :=  $\frac{1}{2} \sqrt{(l-m)(l+m+1)}$  KroneckerDelta [n, m+1] +  
 $\frac{1}{2} \sqrt{(l+m)(l-m+1)}$  KroneckerDelta [n, m-1];  
Jy[l_, n_, m_] :=  
- $\frac{1}{2} i \sqrt{(l-m)(l+m+1)}$  KroneckerDelta [n, m+1] +  
 $\frac{1}{2} i \sqrt{(l+m)(l-m+1)}$  KroneckerDelta [n, m-1];  
Jz[l_, n_, m_] := m KroneckerDelta [n, m];  
  
Lx = Table [Jx[2, n, m], {n, 2, -2, -1}, {m, 2, -2, -1}];  
Ly = Table [Jy[2, n, m], {n, 2, -2, -1}, {m, 2, -2, -1}];  
Lz = Table [Jz[2, n, m], {n, 2, -2, -1}, {m, 2, -2, -1}];  
Lp = Lx + i Ly; Lm = Lx - i Ly;  
I1 = IdentityMatrix [5];
```

Column matrix of $\psi_1, \psi_2, \psi_3, \psi_4, \psi_5$

$$\psi[1] = -\frac{i}{\sqrt{2}} \{1, 0, 0, 0, -1\}; \psi[2] = \frac{i}{\sqrt{2}} \{0, 1, 0, 1, 0\};$$

$$\psi[3] = -\frac{1}{\sqrt{2}} \{0, 1, 0, -1, 0\}; \psi[4] = \frac{1}{\sqrt{2}} \{1, 0, 0, 0, 1\};$$

$$\psi[5] = \{0, 0, 1, 0, 0\};$$

$$\text{Table} [\psi[i]^* \cdot \text{Ix} \cdot \psi[1], \{i, 1, 5\}]$$

$$\{0, 0, i, 0, 0\}$$

$$\text{Table} [\psi[i]^* \cdot \text{Ix} \cdot \psi[2], \{i, 1, 5\}]$$

$$\{0, 0, 0, i, i\sqrt{3}\}$$

$$\text{Table} [\psi[i]^* \cdot \text{Ix} \cdot \psi[3], \{i, 1, 5\}]$$

$$\{-i, 0, 0, 0, 0\}$$

$$\text{Table} [\psi[i]^* \cdot \text{Ix} \cdot \psi[4], \{i, 1, 5\}]$$

$$\{0, -i, 0, 0, 0\}$$

$$\text{Table} [\psi[i]^* \cdot \text{Ix} \cdot \psi[5], \{i, 1, 5\}]$$

$$\{0, -i\sqrt{3}, 0, 0, 0\}$$

Calculation of $L_y.\psi[i]$

Table [$\psi[i]^* \cdot L_y \cdot \psi[1]$, { i , 1, 5}]

{0, - i , 0, 0, 0}

Table [$\psi[i]^* \cdot L_y \cdot \psi[2]$, { i , 1, 5}]

{ i , 0, 0, 0, 0}

Table [$\psi[i]^* \cdot L_y \cdot \psi[3]$, { i , 1, 5}]

{0, 0, 0, i , - $i\sqrt{3}$ }

Table [$\psi[i]^* \cdot L_y \cdot \psi[4]$, { i , 1, 5}]

{0, 0, - i , 0, 0}

Table [$\psi[i]^* \cdot L_y \cdot \psi[5]$, { i , 1, 5}]

{0, 0, $i\sqrt{3}$, 0, 0}

Calculation of $L_z.\psi[i]$

Table [$\psi[i]^* \cdot L_z \cdot \psi[1]$, { i , 1, 5}]

{0, 0, 0, -2 i , 0}

Table [$\psi[i]^* \cdot L_z \cdot \psi[2]$, { i , 1, 5}]

{0, 0, - i , 0, 0}

Table [$\psi[i]^* \cdot L_z \cdot \psi[3]$, { i , 1, 5}]

{0, i , 0, 0, 0}

Table $[\psi[i]^* \cdot Lz \cdot \psi[4], \{i, 1, 5\}]$
{2 i, 0, 0, 0, 0}

Table $[\psi[i]^* \cdot Lz \cdot \psi[5], \{i, 1, 5\}]$
{0, 0, 0, 0, 0}

Calculation of $L+ \cdot \psi[i]$

Table $[\psi[i]^* \cdot Ip \cdot \psi[1], \{i, 1, 5\}]$
{0, 1, i, 0, 0}

Table $[\psi[i]^* \cdot Ip \cdot \psi[2], \{i, 1, 5\}]$
{-1, 0, 0, i, $i\sqrt{3}$ }

Table $[\psi[i]^* \cdot Ip \cdot \psi[3], \{i, 1, 5\}]$
{-i, 0, 0, -1, $\sqrt{3}$ }

Table $[\psi[i]^* \cdot Ip \cdot \psi[4], \{i, 1, 5\}]$
{0, -i, 1, 0, 0}

Table $[\psi[i]^* \cdot Ip \cdot \psi[5], \{i, 1, 5\}]$
{0, $-i\sqrt{3}$, $-\sqrt{3}$, 0, 0}

Calculation of $L- \cdot \psi[i]$

Table $[\psi[i]^* \cdot Im \cdot \psi[1], \{i, 1, 5\}]$
{0, -1, i, 0, 0}

Table $[\psi[i]^* \cdot Im \cdot \psi[2], \{i, 1, 5\}]$
{1, 0, 0, i, $i\sqrt{3}$ }

Table $[\psi[i]^* \cdot Im \cdot \psi[3], \{i, 1, 5\}]$
{-i, 0, 0, 1, $-\sqrt{3}$ }

Table $[\psi[i]^* \cdot Im \cdot \psi[4], \{i, 1, 5\}]$
{0, -i, -1, 0, 0}

Table $[\psi[i]^* \cdot Im \cdot \psi[5], \{i, 1, 5\}]$
{0, $-i\sqrt{3}$, $\sqrt{3}$, 0, 0}

7. The energy diagram of Cu^{2+} with $(3d)^9$ electron configuration: Rule-1

Here we consider the energy level of $(3d)^9$ for Cu^{2+} . There are nine electrons, i.e., one short of filled 3d shell, where $(3d)^9 = (3d)^{10} + 1$ hole (positive charge)

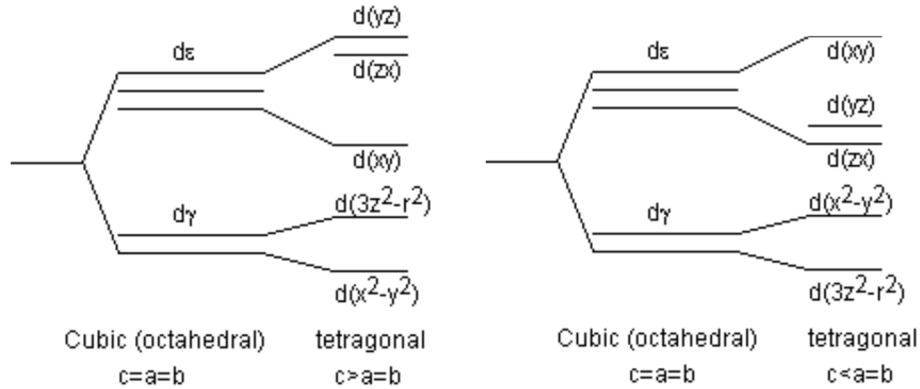


Fig.16 Energy diagram for $(3d)^9$ in the octahedral and tetragonal cases for (i) $c > a = b$. (ii) $c < a = b$.

In the $(3d)^9$ electron configuration, we have $(3d)^9$: $2S+1 = 2$, $2L+1 = 5$ ($L = 2$). The ground state is a Kramers doublet. Since $S = 1/2$, there is no single ion anisotropy (see 12.1 for detail). A full shell of electrons has a charge cloud which is spherically symmetric so that removal of one electron leaves a distributed charge deficiency coincident with the space charge of the electron moved. This gap or “hole” behaves like a single positively charged electron.

For the $(3d)^9$ ion in an octahedral crystal field, the argument therefore proceeds as for $3d^1$ except the $d\epsilon$ and $d\gamma$ levels will now be reversed in the energy level diagram because the ion has a lesser energy when the lobes of the positive hole’s wavefunction are directed towards neighboring negative ions rather than between the ions. In some cases the derivation from regularity might arise spontaneously from the crystal-field effect themselves because, if the ground-state in a regular field is orbitally degenerate, slight distortion of the environment can lower the ground-state energy and at the same time remove some degeneracy, pushing some levels up and other down. Both the doubly degenerate ground-state and the triply-degenerate level are split into two. If the distortion in the z direction, the $d(yz)$ and $d(zx)$ states of the triplet remain symmetrically disposed and, though displaced upwards in energy, they remain degenerate. The $d(xy)$ state, on the other hand, is displaced downward, in energy, and the center of gravity of the triplet remains unchanged to the first order. The $d(3z^2-r^2)$ and $d(x^2-y^2)$ states of the unperturbed ground-state are not symmetrical with respect to the z -axis and are separated by the distortion, $d(3z^2-r^2)$ becoming an orbitally non-degenerate ground state.

In conclusion, The energy diagram of $(3d)^9$ and $(3d)^1$ configuration are inverted in relation to each other because $(3d)^9$ may be treated as a $(3d)^1$ positive hole in a filled $(3d)^{10}$ shell.

8. Energy diagram of $(3d)^n$ electron configuration

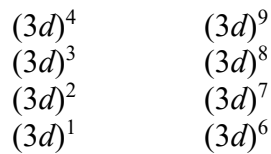
8.1. Rule-2

Using the Hund’s rule and the energy levels of $(3d)^1$ electron configuration, we consider the ground state of the $(3d)^n$ ($n \geq 2$) electron configuration.



The ground state of an ion with a half-filled shell has an orbital moment $L = 0$, since all the $3d$ orbital states are singly occupied. The additional electron in the $3d^6$ therefore leave the ion in a D state just as for a $3d^1$ configuration, and the crystal-field levels are the same as for $3d^1$.

Splitting in the energy-level diagram of the ground state of $3d^n$ ion due to octahedral fields and tetragonal fields.



((Difference appears when spin-orbit perturbations are concerned.))

8.2. Ground state for $(3d)^n$ electron configuration ($n > 1$)

We assume that the Hund's rule is valid for $n \geq 2$: $V_H > V_{cr}$ (weak field case), where V_H is the electron-electron interaction and V_{cr} is the crystal field.

(i)

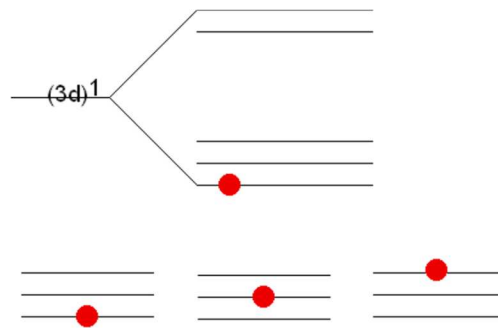


Fig.17(a) Ground state of $(3d)^1$: orbital triplet, where the red circle denote electron up-spin state. $d\varepsilon^1$

(ii)

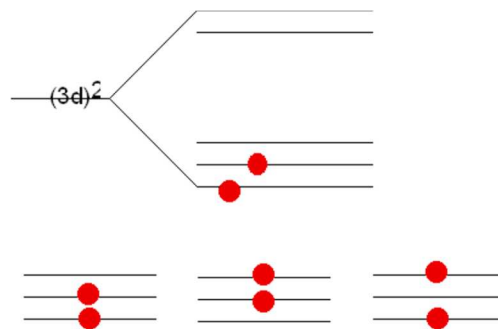


Fig.17(b) Ground state of $(3d)^2$: orbital triplet. $d\varepsilon^2$

(iii)

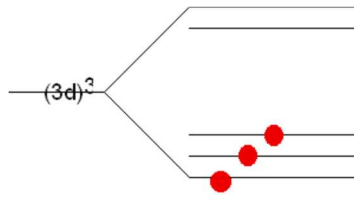


Fig.17(c) Ground state of $(3d)^3$: orbital singlet. $d\varepsilon^3$. The quenching of the orbital angular momentum

(iv)

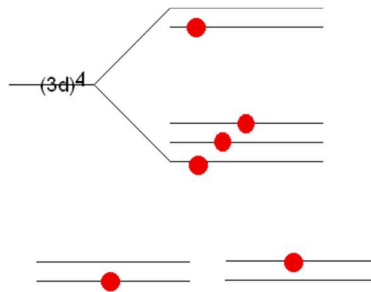


Fig.17(d) Ground state of $(3d)^4$: orbital doublet. The possibility of Jahn-Teller effect. $d\varepsilon^3d\gamma^1$

(v)

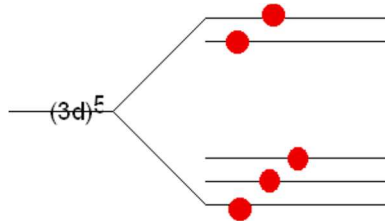


Fig.17(e) Ground state of $(3d)^5$: orbital singlet. $d\varepsilon^3d\gamma^2$. The quenching of the orbital angular momentum

(vi)

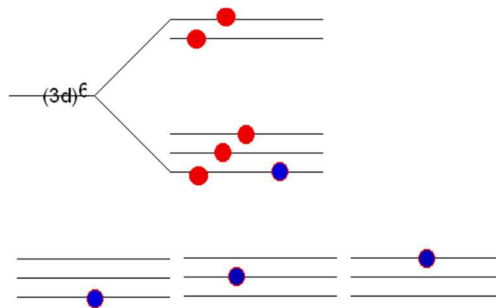


Fig.17(f) Ground state of $(3d)^6$: orbital triplet. $d\varepsilon^4d\gamma^2$. The red circle and blue circle denote electron up-state and down-state.

(vii)

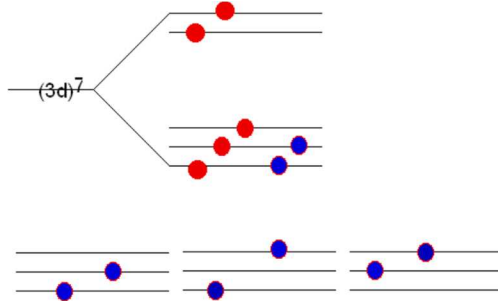


Fig.17(g) Ground state of $(3d)^7$: orbital triplet. $d\varepsilon^5d\gamma^2$.

(viii)

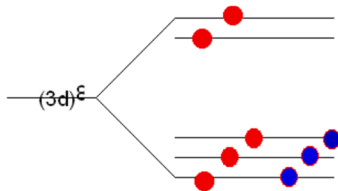


Fig.17(h) Ground state of $(3d)^8$: orbital singlet. $d\varepsilon^6d\gamma^2$. The quenching of the orbital angular momentum

(ix)

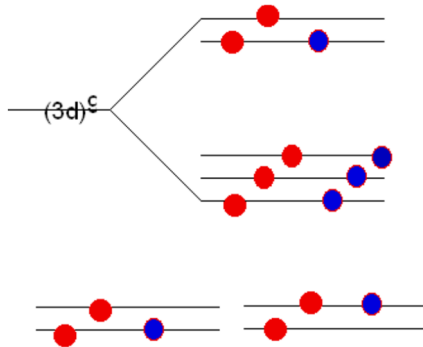


Fig.17(i) Ground state of $(3d)^9$: orbital doublet. $d\varepsilon^6d\gamma^3$. The possibility of the Jahn-Teller effect

8.4. Excited states for $(3d)^2$ electron configuration

We consider the excited states of the $(3d)^2$ electron configuration. We take into account of only the Hund's first law (exchange interaction) (parallel spin electrons are occupies from lowest energy).

(i) Ground state: orbital triplet. The degeneracy is ${}^3C_1 = 3$

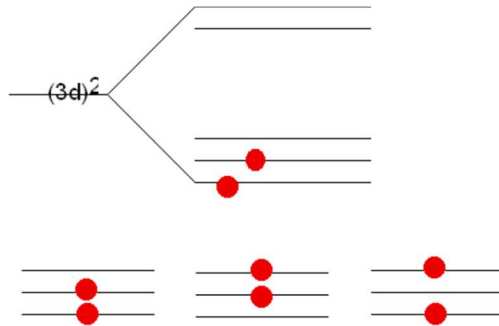


Fig.18(a) Ground state of $(3d)^2$ electron configuration (one-electron model).

(ii) First excited state. The degeneracy is ${}^2C_1 {}^3C_1 = 2 \times 3 = 6$

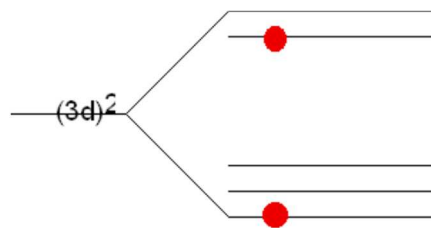


Fig.18(b) Excited state of $(3d)^2$ electron configuration (one-electron model).

(iii) Second excited state. the orbital singlet.

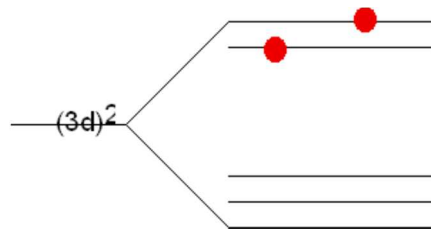


Fig.18(c) Second excited state of $(3d)^2$ electron configuration (one-electron model).

In Summary we have the following energy diagram for $(3d)^2$. Note that when the Hund's second law is also taken into account, the six degeneracy of the first excited state is split into the two triplet states.

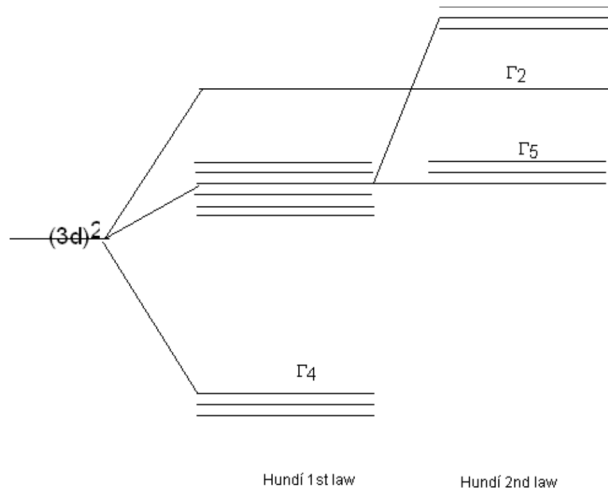


Fig.18(d) Energy diagram of $(3d)^2$ electron configuration (two-electrons system). Γ_4 : the ground state (orbital triplet), Γ_5 : the first excited state (orbital triplet), Γ_2 : the second excited state (orbital singlet).

8.5. Excited states for $(3d)^3$ electron configuration

- Ground state Orbital triplet: ${}^3C_1 = 3$
- First excited state 6 states (splitting into two orbital triplet due to the Hund's 2nd law)
 ${}^3C_1 \times {}^2C_1 = 6$
- Second excited state Orbital triplet. ${}^3C_1 = 3$.

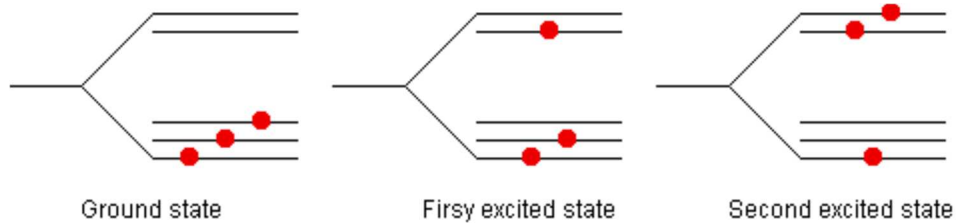


Fig.19 (a) Ground state, the first excited state, and the second excited state of $(3d)^3$ electron configuration (one-electron model).

In summary we obtain the following energy diagram

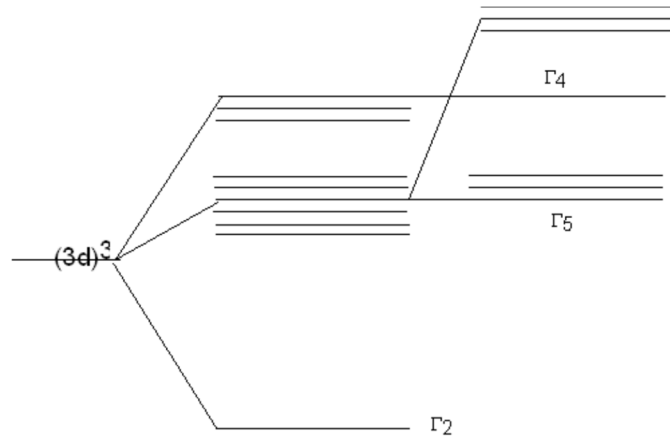


Fig.19(b) Energy diagram of $(3d)^3$ electron configuration (three-electrons system). Γ_2 (orbital singlet), Γ_5 and Γ_4 (orbital triplets)

8.5. Excited states of $(3d)^1$ electron configuration

Ground state	Orbital triplet ($3C_1 = 3$)
Excited state	Orbital doublet ($2C_1 = 2$).

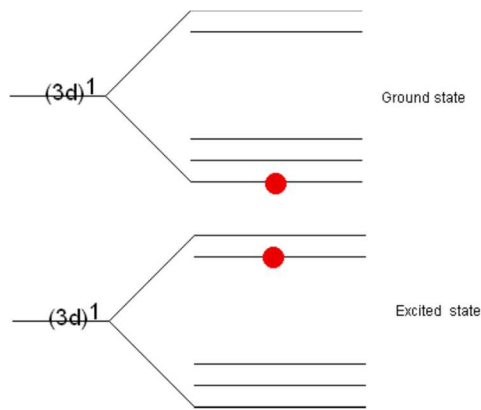


Fig.20(a) Ground state and excited states of $(3d)^1$ electron configuration (one electron model)

In summary, we have

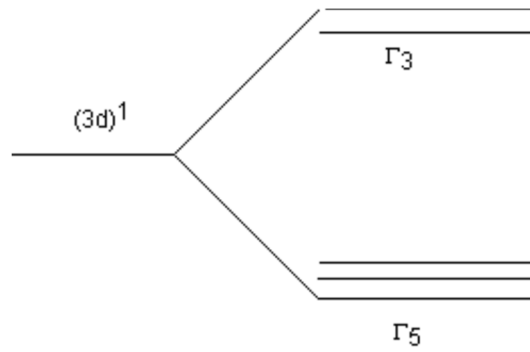


Fig.20(b) Ground state and excited states of $(3d)^1$ electron configuration. The energy levels are the same as shown in Fig.20(a).

8.6. Excited states of $(3d)^4$ electron configuration

Ground state	Orbital doublet.	${}^2C_1 = 2.$
Excited state	Orbital triplet	${}^3C_1 = 3.$

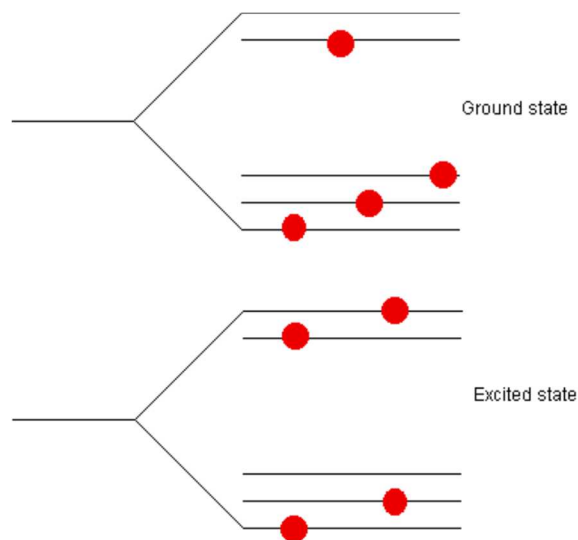


Fig.21(a) Ground state and excited states of $(3d)^4$ electron configuration (one electron model)

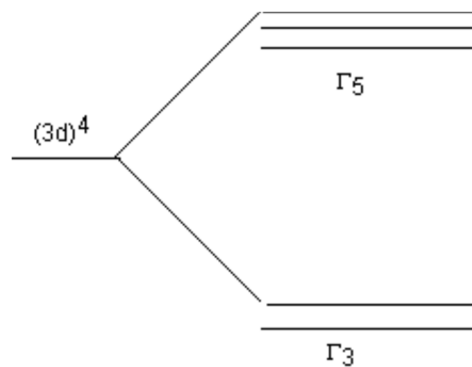


Fig.21(b) Ground state and excited states of $(3d)^4$ electron configuration (four electrons system).

8.7. Energy diagram: application of rule-1 and rule-2

Crystal field energy levels for orbital electrons in the octahedral (cubic) and tetragonal fields have five symmetry types called irreducible representations.

Singlet	$A_1 (\Gamma_1)$,
singlet	$A_2 (\Gamma_2)$,
doublet	$E (\Gamma_3)$,
triplet	$T_1 (\Gamma_4)$,
triplet	$T_2 (\Gamma_5)$.

One often uses the notation A_{1g} , T_{2g} , E_g , and so on, where *g* stands for *gerade* and means that the wavefunction is asymmetric under inversion.

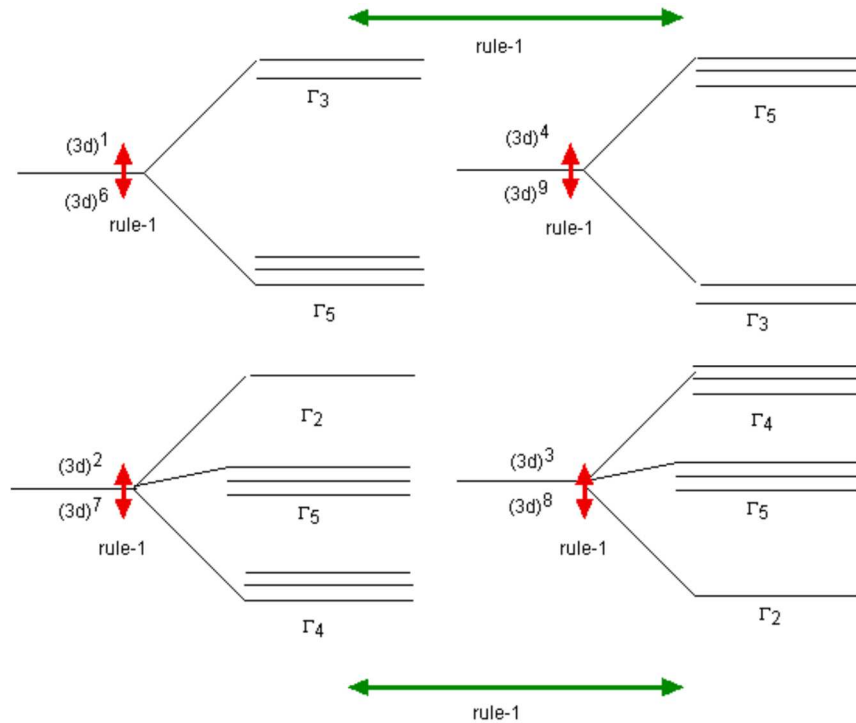


Fig.22 Energy diagram of $(3d)^n$ ($n = 1, 2, 3, 4$) with the rule-1 and rule-2. Γ_4 and Γ_5 triplets can be represented by a fictitious orbital angular momentum.

9. Jahn-Teller effect

We now consider the energy diagram of Cu^{2+} for the $(3d)^9$ electron configuration. The energy level of Cu^{2+} consists of ground state (orbital doublet Γ_3 , $d\gamma$) and the excited state (orbital triplet Γ_5 , $d\epsilon$) in the octahedral field ($c = a = b$). The ground state is split into the two orbital singlets [$d(x^2 - y^2)$ and $d(3z^2 - r^2)$] in the tetragonal field, as a result of the lattice distortion ($c > a = b$). Here the energy level of $d(x^2 - y^2)$ is lower than that of $d(3z^2 - r^2)$. In this case, there are two contributions to the total energy. One is the energy loss due

to the lattice distortion (the increase of the distance c). The other is the energy gain due to the lowering of the energy level of the ground state. If the energy gain is larger than the energy loss, a spontaneous displacement occurs (Jahn-Teller effect).

10. Low spin and high spin states

We consider the case of Fe^{2+} . Isolated Fe^{2+} has $(3d)^6$ electron configuration. $(3d)^5$ has five parallel spins (up). The remaining one electron for 3d has a down-spin, and takes $l = 2$ according to the Hund rule ($S = 2, L = 2$).

((Weak crystal field))

When Fe^{2+} is a part of FeO , the orbital of the remaining one 3d electron is influenced by 6 O^{2-} , or one 3d electron is located in the octahedral crystal field. In this case, the energy level splits into the d_e and d_g levels. 1(3d) electron occupies the energy level of d_e (down-spin). In this case we have $S = 2$. We call this state as a high spin state. This is the case of weak crystal field that the Hund field V_H is larger than V_c .

((Strong crystal field))

What happens when the crystal field is strong ($V_{cr} > V_H$). In this case all 6 states in the d_e are occupied by 3 up-spin states and 3-spin down states since $V_{cr} > V_H$. Then we have the $S = 0$ (we call this low spin state).

11. Spin Hamiltonian of spin systems with the orbital singlet as a ground state

11.1. Pryce spin Hamiltonian

Now we apply the perturbation theory (degenerate case) where the *orbital ground state is singlet*.¹⁶ The Hamiltonian is described by

$$\hat{H} = \hat{H}_c + \hat{H}', \quad (11.1)$$

where \hat{H}_c is the unperturbed Hamiltonian of the system under the octahedral crystal field. The perturbation \hat{H}' is given by

$$\hat{H}' = \lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{H}, \quad (11.2)$$

where the first term is the spin-orbit interaction and the second term is the Zeeman energy. $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are the operators of the orbital and spin angular momentum in the quantum mechanics. We now transform \hat{H}' into the so-called spin Hamiltonian by a method proposed by Pryce, where the orbital dependence is projected out.

Let us evaluate the expectation value of \hat{H}' for a nondegenerate ground state (orbital singlet $|\Psi_0\rangle$).³ To the second order perturbation for the non-degenerate case (see the

Appendix for the perturbation theory)

Here

$$\langle \Psi_0 | \hat{H}' | \Psi_0 \rangle = \langle \Psi_0 | \lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{H} | \Psi_0 \rangle = \langle \Psi_0 | \mu_B (2\hat{\mathbf{S}}) \cdot \mathbf{H} | \Psi_0 \rangle = 2\mu_B \hat{\mathbf{S}} \cdot \mathbf{H}$$

$$\begin{aligned}\langle \Gamma', \gamma' | \hat{H} | \Psi_0 \rangle &= \langle \Gamma', \gamma' | \lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} | \Psi_0 \rangle \\ &= \lambda S_\mu \langle \Gamma', \gamma' | \hat{L}_\mu | \Psi_0 \rangle + \mu_B H_\mu \langle \Gamma', \gamma' | \hat{L}_\mu | \Psi_0 \rangle\end{aligned}$$

We use the quenching of the orbital angular momentum for the orbital singlet.

$$\begin{aligned}H(\hat{\mathbf{S}}) &= 2\mu_B \hat{\mathbf{S}} \cdot \mathbf{H} \\ &- \sum_{\Gamma', \gamma'} \frac{[\lambda S_\mu \langle \Psi_0 | \hat{L}_\mu | \Gamma', \gamma' \rangle + \mu_B H_\mu \langle \Psi_0 | \hat{L}_\mu | \Gamma', \gamma' \rangle][\lambda S_\nu \langle \Gamma', \gamma' | \hat{L}_\nu | \Psi_0 \rangle + \mu_B H_\nu \langle \Gamma', \gamma' | \hat{L}_\nu | \Psi_0 \rangle]}{E(\Gamma', \gamma') - E_0}\end{aligned}\quad (11.3)$$

We introduce the notation

$$\Lambda_{\mu\nu} = \sum_{\Gamma', \gamma'} \frac{\langle \Psi_0 | \hat{L}_\mu | \Gamma', \gamma' \rangle \langle \Gamma', \gamma' | \hat{L}_\nu | \Psi_0 \rangle}{E(\Gamma', \gamma') - E_0}.\quad (11.4)$$

$$H(\hat{\mathbf{S}}) = 2\mu_B \hat{\mathbf{S}} \cdot \mathbf{H} - \sum_{\mu, \nu} [\lambda^2 \Lambda_{\mu\nu} \hat{S}_\mu \hat{S}_\nu + \mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu + \lambda \mu_B \Lambda_{\mu\nu} (H_\mu \hat{S}_\nu + H_\nu \hat{S}_\mu)],\quad (11.5)$$

or

$$H(\hat{\mathbf{S}}) = \sum_{\mu, \nu} (\mu_B g_{\mu\nu} H_\mu \hat{S}_\nu - \lambda^2 \Lambda_{\mu\nu} \hat{S}_\mu \hat{S}_\nu - \mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu),\quad (11.6)$$

where $E(\Gamma', \gamma') - E_0$ is the energy gap between the ground state and the excited states.

$$g_{\mu\nu} = 2(\delta_{\mu\nu} - \lambda \Lambda_{\mu\nu}).\quad (11.7)$$

What is the physical meaning of the above spin Hamiltonian?

- (i) The g tensor which is different from 2, because of spin-orbit interaction.
- (ii) The second term represents the single-ion anisotropy. Note that $\Lambda_{\mu\nu}$ reflects the symmetry of the system.

We neglect the last term which is related to the Van Vleck susceptibility. We also assume that

$$\mathbf{\Lambda} = \begin{pmatrix} \Lambda_{xx} & 0 & 0 \\ 0 & \Lambda_{yy} & 0 \\ 0 & 0 & \Lambda_{zz} \end{pmatrix}.\quad (11.8)$$

$$\begin{cases} g_{xx} = 2(1 - \lambda\Lambda_{xx}) \\ g_{yy} = 2(1 - \lambda\Lambda_{yy}) \\ g_{zz} = 2(1 - \lambda\Lambda_{zz}) \end{cases} \quad (11.9)$$

The spin Hamiltonian should reflect the symmetry of the crystal field. Then the spin Hamiltonian can be written as

$$\begin{aligned} \hat{H}(\hat{\mathbf{S}}) &= -\lambda^2(\Lambda_{zz}\hat{S}_z^2 + \Lambda_{xx}\hat{S}_x^2 + \Lambda_{yy}\hat{S}_y^2) + \mu_B(g_{xx}\hat{S}_xH_x + g_{yy}\hat{S}_yH_y + g_{zz}\hat{S}_zH_z) \\ &= -\lambda^2[\Lambda_{zz} - \frac{1}{2}(\Lambda_{xx} + \Lambda_{yy})][\hat{S}_z^2 - \frac{1}{3}S(S+1)] - \lambda^2\frac{1}{2}(\Lambda_{xx} - \Lambda_{yy})(\hat{S}_x^2 - \hat{S}_y^2) \\ &\quad + \mu_B(g_{xx}\hat{S}_xH_x + g_{yy}\hat{S}_yH_y + g_{zz}\hat{S}_zH_z) \end{aligned} \quad (11.10)$$

Note that for simplicity we use the unit of $\hbar = 1$. We put

$$\delta = -\lambda^2[\Lambda_z - \frac{1}{2}(\Lambda_x + \Lambda_y)], \quad (11.11)$$

$$\varepsilon = -\lambda^2(\Lambda_x - \Lambda_y)/2. \quad (11.12)$$

Then the effective spin Hamiltonian $\hat{H}(\hat{\mathbf{S}})$ is described as

$$\hat{H}(\hat{\mathbf{S}}) = \delta[\hat{S}_z^2 - \frac{1}{3}S(S+1)] + \varepsilon(\hat{S}_x^2 - \hat{S}_y^2) + \mu_B(g_{xx}\hat{S}_xH_x + g_{yy}\hat{S}_yH_y + g_{zz}\hat{S}_zH_z) \quad (11.13)$$

Note that an important experimental fact is that the crystal-field parameters (δ , ε , and g) do not change appreciably for the same types of the systems.

11.2 g-factors and the single ion anisotropy D

A. Definition of g-factors

We define $g_x = g_{xx}$, $g_y = g_{yy}$, and $g_{zz} = g_z$.

$$\begin{cases} g_x = 2(1 - \lambda\Lambda_x) & \Lambda_x = \frac{1}{\lambda}(1 - \frac{g_x}{2}) \\ g_y = 2(1 - \lambda\Lambda_y) & \Rightarrow \Lambda_y = \frac{1}{\lambda}(1 - \frac{g_y}{2}) \\ g_z = 2(1 - \lambda\Lambda_z) & \Lambda_z = \frac{1}{\lambda}(1 - \frac{g_z}{2}) \end{cases} \quad (11.14)$$

The single ion anisotropy constant D is given by

$$\begin{aligned}
D &= -\lambda^2 \left[\Lambda_z - \frac{1}{2}(\Lambda_x + \Lambda_y) \right] \\
&= -\frac{\lambda^2}{\lambda} \left[\left(1 - \frac{g_z}{2} \right) - \frac{1}{2} \left(2 - \frac{g_x}{2} - \frac{g_y}{2} \right) \right] \\
&= -\lambda \left[-\frac{g_z}{2} + \frac{1}{4}(g_x + g_y) \right] \\
&= \frac{\lambda}{2} \left[g_z - \frac{1}{2}(g_x + g_y) \right]
\end{aligned} \tag{11.15}$$

We assume that $g_z = g_c$, $g_x = g_y = g_a$ for simplicity. The constant D is rewritten as

$$D = \frac{\lambda}{2}(g_c - g_a). \tag{11.16}$$

Note that the sign of the spin-orbit interaction constant λ is as follows,

$$\begin{cases} \lambda > 0 & (\text{less than half; } (3d)^n \text{ } n < 5) \\ \lambda < 0 & (\text{more than half; } (3d)^n \text{ } n > 5) \end{cases}$$

Then we have

$$\begin{aligned}
\text{If } \lambda > 0, \text{ then } g_c > g_a & \Rightarrow D > 0. \\
\text{If } \lambda < 0, \text{ then } g_c > g_a & \Rightarrow D < 0.
\end{aligned}$$

Note that the g -value of the free electron is not precisely 2. There are quantum electrodynamics corrections which leads to the value $g = 2.0023193043622$.

B. g -factors in Cu^{2+} ion in the tetragonal field ($c > a = b$)

For Cu^{2+} ion in the tetragonal field ($c > a = b$), the ground state is $|\psi_4\rangle$ (orbital singlet). In this case the tensor components (see Fig.16 for the energy diagram for Cu^{2+} ion).

$$\begin{aligned}
\Lambda_\mu &= \frac{\langle \psi_4 | \hat{L}_\mu | \psi_5 \rangle \langle \psi_5 | \hat{L}_\mu | \psi_4 \rangle}{E_5 - E_4} + \frac{\langle \psi_4 | \hat{L}_\mu | \psi_3 \rangle \langle \psi_3 | \hat{L}_\mu | \psi_4 \rangle}{E_3 - E_4} \\
&+ \frac{\langle \psi_4 | \hat{L}_\mu | \psi_1 \rangle \langle \psi_1 | \hat{L}_\mu | \psi_4 \rangle}{E_{1,2} - E_4} + \frac{\langle \psi_4 | \hat{L}_\mu | \psi_2 \rangle \langle \psi_2 | \hat{L}_\mu | \psi_4 \rangle}{E_{1,2} - E_4},
\end{aligned} \tag{11.17}$$

where $\mu = x, y$ and z . Noting that

$$\hat{L}_x |\psi_4\rangle = -i|\psi_2\rangle, \quad \hat{L}_y |\psi_4\rangle = -i|\psi_3\rangle, \quad \hat{L}_z |\psi_4\rangle = 2i|\psi_1\rangle.$$

(we use the unit of $\hbar = 1$), we have

$$\begin{aligned}
 \Lambda_x &= \frac{\langle \psi_4 | \hat{L}_x | \psi_2 \rangle \langle \psi_2 | \hat{L}_x | \psi_4 \rangle}{E_2 - E_4} = \frac{1}{E_2 - E_4} \\
 \Lambda_y &= \frac{\langle \psi_4 | \hat{L}_y | \psi_3 \rangle \langle \psi_3 | \hat{L}_y | \psi_4 \rangle}{E_3 - E_4} = \frac{1}{E_3 - E_4} \\
 \Lambda_z &= \frac{\langle \psi_4 | \hat{L}_z | \psi_1 \rangle \langle \psi_1 | \hat{L}_z | \psi_4 \rangle}{E_1 - E_4} = \frac{4}{E_1 - E_4}
 \end{aligned} \tag{11.18}$$

Then the g -values are calculated as

$$\begin{aligned}
 g_z &= 2\left(1 - \frac{4\lambda}{E_1 - E_4}\right) \\
 g_x &= 2\left(1 - \frac{\lambda}{E_2 - E_4}\right), \\
 g_y &= 2\left(1 - \frac{\lambda}{E_3 - E_4}\right)
 \end{aligned} \tag{11.19}$$

where $\lambda (\approx -850 \text{ cm}^{-1})$ and $E_2 = E_3 > E_1 > E_5 > E_4$. We find that

$$g_x = g_y < g_z.$$

11.3. Ni^{2+}

As a typical example, we consider the case of $\text{Ni}^{2+} [(3d)^8; S = 1, L = 3]$ under the octahedral crystal field. The energy diagram consists of an orbital singlet state (T_2) as a ground state and an orbital triplet (T_3). The energy difference between the ground state and the excited state is 1 eV and is much larger than the magnitude of the spin-orbit coupling constant $\lambda (= -335 \text{ cm}^{-1} = -0.0415 \text{ eV})$, Note that $1 \text{ meV} = 8.0655 \text{ cm}^{-1}$.

(i) Since the ground state is the orbital singlet, the quenching of the orbital angular momentum occurs.

(ii) The spin degeneracy is $(2S + 1) = 3$. $|S, m_s\rangle$ with $S = 1$, and $m_s = 1, 0$, and -1 .

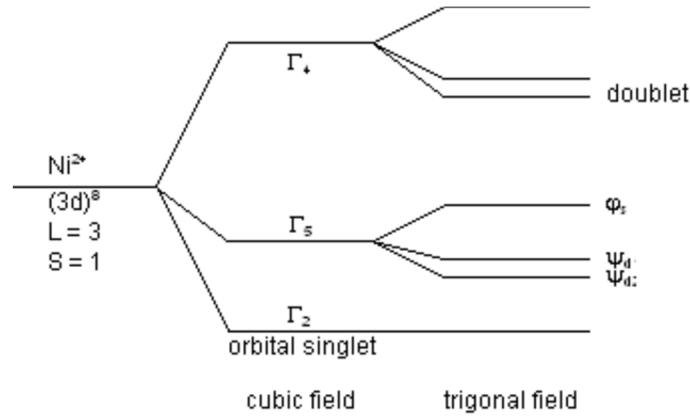


Fig.23 Crystal-field splitting of Ni^{2+} ion ground state in the octahedral and tetragonal fields.

In the ground-orbital singlet, the mean value of orbital angular momentum is zero and the value of spin $S = 1$. The spin anisotropy arises only as a 2nd-order effect through the combined effect of spin-orbit coupling and trigonal field within the upper states which are linked with the ground state in the second order perturbation. For a trigonal distortion, we expect the anisotropy to be adequately represented by a term DS_z^2 .

11.4 Cr^{3+}

$\text{Cr}^{3+} (3d^3)$ has a ground state 4F . In an octahedral field, the sevenfold orbital degeneracy ($2L+1 = 7$) is removed, and the levels are split into a lower orbital singlet (Γ_2) and two higher lying orbital triplets (Γ_5, Γ_4). The low-lying singlet has a fourfold spin degeneracy ($2S+1 = 4, S = 3/2$). It is not removed even by the combination action of the octahedral and spin-orbit coupling, forming two Kramers doublets (see the detail in Sec.12). It can be removed only by the external magnetic field.

12. Spin Hamiltonian for $S = 1/2, 1, 3/2, 2$ and $5/2$

12.1 $S = 1/2$

For $S = 1/2$, the spin operators are described by

$$\begin{cases} \hat{S}_x = \frac{1}{2} \sigma_x \\ \hat{S}_y = \frac{1}{2} \sigma_y \\ \hat{S}_z = \frac{1}{2} \sigma_z \end{cases} \quad (12.1)$$

where the Pauli spin matrix is given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (12.2)$$

$$\begin{cases} \sigma_x^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ \sigma_y^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ \sigma_z^2 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{cases} \quad (12.3)$$

$$\hat{S}_z^2 = \frac{1}{4} \sigma_z^2 = \frac{1}{4}, \quad \hat{S}_x^2 = \hat{S}_y^2 = \frac{1}{4}. \quad (12.4)$$

Then Hamiltonian ($S = 1/2$) can be described as

$$\hat{H}(\hat{\mathbf{S}}) = \mu_B (g_x \hat{S}_x H_x + g_y \hat{S}_y H_y + g_z \hat{S}_z H_z). \quad (12.5)$$

We note that there is no single ion anisotropy for $S = 1/2$.

12.2. $S=1$

A. Eigenvalue problem for $S = 1$

For $S = 1$ in the case of $(3d)^8$, Ni^{2+} ion), the spin operators are described by (3x3) spin matrices,

$$\hat{S}_x = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix}, \quad \hat{S}_y = \begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ 0 & \frac{i}{\sqrt{2}} & 0 \end{pmatrix}, \quad \hat{S}_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \quad (12.6)$$

Then

$$\hat{S}_x^2 = \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}, \quad \hat{S}_y^2 = \begin{pmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}, \quad \hat{S}_z^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (12.7)$$

Here we consider the eigenvalue problem for the effective spin Hamiltonian given by

$$\hat{H} = \delta [\hat{S}_z^2 - \frac{1}{3} S(S+1)] + \varepsilon (\hat{S}_x^2 - \hat{S}_y^2). \quad (12.8)$$

We have the determinant given by

$$\Delta = \det(\hat{H} - W\hat{I}) = \begin{vmatrix} \frac{\delta}{3} - W & 0 & \varepsilon \\ 0 & -\frac{2\delta}{3} - W & 0 \\ \varepsilon & 0 & \frac{\delta}{3} - W \end{vmatrix} = 0, \quad (12.9)$$

or

$$W = -\frac{2}{3}\delta, \frac{\delta}{3} - \varepsilon, \frac{\delta}{3} + \varepsilon$$

where W is the energy eigenvalue. For Ni^{2+} it is known that $\delta = \varepsilon = 1 \text{ cm}^{-1}$.

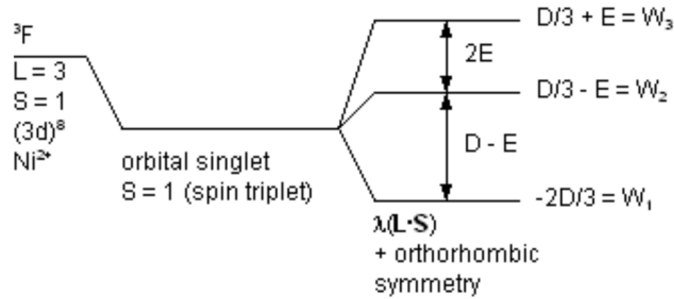


Fig.24 Energy level of $(3d)^8 \text{Ni}^{2+}$ ion, where $D = \delta$ and $E = \varepsilon$.

The ground state with spin triplet (orbital singlet) is split into three spin singlets due to the spin-orbit interaction.

What is the wave function of the ground state?

For $W = W_1 = -\frac{2}{3}\delta,$

$$\begin{matrix} |1\rangle \\ |0\rangle \\ |-1\rangle \end{matrix} \begin{pmatrix} |1\rangle & |0\rangle & |-1\rangle \\ \frac{\delta}{3} - W_1 & 0 & \varepsilon \\ 0 & -\frac{2\delta}{3} - W_1 & 0 \\ \varepsilon & 0 & \frac{\delta}{3} - W_1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad (12.10)$$

or

$$\begin{pmatrix} \delta & 0 & \varepsilon \\ 0 & 0 & 0 \\ \varepsilon & 0 & \delta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad (12.11)$$

or

$$\delta c_1 + \varepsilon c_3 = 0$$

$$\varepsilon c_1 + \delta c_3 = 0$$

$$c_1 = c_3 = 0$$

$$\psi_1 = |0\rangle$$

For $W = W_2 = \frac{\delta}{3} - \varepsilon$

$$\begin{pmatrix} \frac{\delta}{3} - W_2 & 0 & \varepsilon \\ 0 & -\frac{2\delta}{3} - W_2 & 0 \\ \varepsilon & 0 & \frac{\delta}{3} - W_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

or

$$\begin{pmatrix} \varepsilon & 0 & \varepsilon \\ 0 & -\delta + \varepsilon & 0 \\ \varepsilon & 0 & \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \quad (12.12)$$

$$\varepsilon(c_1 + c_3) = 0 \text{ and } c_2 = 0 \quad \therefore c_3 = -c_1$$

$$\psi_2 = \frac{1}{\sqrt{2}}(|1\rangle - |-1\rangle)$$

For $W = W_3 = \frac{\delta}{3} + \varepsilon$,

$$\begin{pmatrix} \frac{\delta}{3} - W_3 & 0 & \varepsilon \\ 0 & -\frac{2\delta}{3} - W_3 & 0 \\ \varepsilon & 0 & \frac{\delta}{3} - W_3 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

or

$$\begin{pmatrix} -\varepsilon & 0 & \varepsilon \\ 0 & -\delta - \varepsilon & 0 \\ \varepsilon & 0 & -\varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad (12.13)$$

$$-\varepsilon c_1 + \varepsilon c_3 = 0 \text{ and } c_2 = 0 \quad \therefore c_1 = c_3$$

$$\psi_3 = \frac{1}{\sqrt{2}}(|1\rangle + |-1\rangle)$$

Since the ground state is a spin singlet

$$\begin{array}{l} \text{—————} \quad |\psi_3\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |-1\rangle) \\ \text{—————} \quad |\psi_2\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |-1\rangle) \\ \text{—————} \quad |\psi_1\rangle = |0\rangle \end{array}$$

we find that the quenching of the spin angular momentum occurs in the system

$$\langle \psi_1 | S_z | \psi_1 \rangle = \langle 0 | S_z | 0 \rangle = 0. \quad (12.14)$$

B. Magnetic susceptibility with the quenching of the spin angular momentum

What is the susceptibility of the system for H/z ? We start with this formula with $H = H_0$,

$$\chi = \frac{N_A k_B T}{H_0} \frac{\partial}{\partial H_0} \ln Z, \quad (12.15)$$

Noting that

$$W_1 = -\frac{2}{3}\delta, \quad W_2 = \frac{\delta}{3} - \sqrt{\varepsilon^2 + g^2 \mu_B^2 H_0^2} \quad W_3 = \frac{\delta}{3} + \sqrt{\varepsilon^2 + g^2 \mu_B^2 H_0^2},$$

the partition function Z can be estimated as

$$Z = e^{\frac{2}{3}\beta\delta} + e^{-\frac{\delta}{3}\beta} [e^{\beta\sqrt{\varepsilon^2 + g^2 \mu_B^2 H_0^2}} + e^{-\beta\sqrt{\varepsilon^2 + g^2 \mu_B^2 H_0^2}}]$$

Then we have

$$\ln Z = -\frac{\delta}{3}\beta + \ln\left[e^{\beta\delta} + 2\cosh\beta\sqrt{\varepsilon^2 + g^2\mu_B^2H_0^2}\right]$$

Then the susceptibility is given by

$$\chi = \frac{2N_A g^2 \mu_B^2}{|\varepsilon|} \frac{\sinh(\beta|\varepsilon|)}{(e^{\beta\delta} + 2\cosh(\beta|\varepsilon|))} \quad (12.16)$$

at $H_0 = 0$. In the limit of $|\varepsilon| \rightarrow 0$,

$$\chi = \frac{2N_A g^2 \mu_B^2}{(2 + e^{\delta/k_B T})k_B T} = \frac{3g^2}{4} \frac{1}{T(2 + e^{T_0/T})}, \quad (12.17)$$

where $\delta = k_B T_0$, and $N_A \mu_B^2 / (3k_B) = 0.125049 \approx 1/8$ emu/(mol K). N_A is the Avogadro number and k_B is the Boltzmann constant. When we assume that $g = 2$, we have the T dependence of the susceptibility shown here, where T_0 is changed as a parameter. The susceptibility has a maximum at $T/T_0 = 0.6835$.

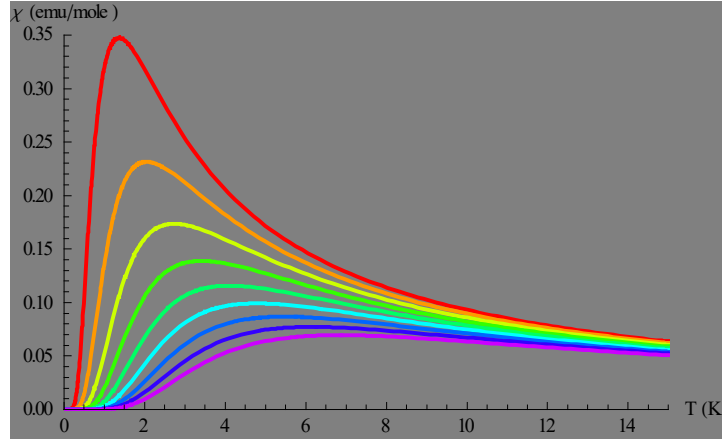


Fig.25 Temperature dependence of the susceptibility for $S = 1$. $T_0 = \delta/k_B = 2$ (red), 3, 4, 5, 6, 7, 8, 9, 10 K (purple).

At low temperature, χ becomes zero, because of the factor $e^{\delta/k_B T}$. The energy of ground state does not change with the magnetic field. (the system is in the ground state with singlet.)

C. Mathematica program: energy diagram of the spin Hamiltonian with $S = 1$ in the presence of magnetic field (the general case)

As an example of the application of the spin Hamiltonian, we consider a spin $S = 1$ in an axially symmetric system with an external magnetic field $\mathbf{H} = (H_x, H_y, H_z)$.

The energy level of the spin Hamiltonian with $S = 1$

$$H = g\mu_B (H_x S_x + H_y S_y + H_z S_z) + \delta [S_z^2 - S(S+1)/3] + \epsilon (S_x^2 - S_y^2)$$

```

Clear["Global`*"];
Jx[l_, n_, m_] :=
  1/2 Sqrt[(l - m) (l + m + 1)] KroneckerDelta[n, m + 1] +
  1/2 Sqrt[(l + m) (l - m + 1)] KroneckerDelta[n, m - 1];
Jy[l_, n_, m_] :=
  -1/2 I Sqrt[(l - m) (l + m + 1)] KroneckerDelta[n, m + 1] +
  1/2 I Sqrt[(l + m) (l - m + 1)] KroneckerDelta[n, m - 1];
Jz[l_, n_, m_] := m KroneckerDelta[n, m]

Sx = Table[Jx[1, n, m], {n, 1, -1, -1}, {m, 1, -1, -1}];
Sy = Table[Jy[1, n, m], {n, 1, -1, -1}, {m, 1, -1, -1}];
Sz = Table[Jz[1, n, m], {n, 1, -1, -1}, {m, 1, -1, -1}];
I1 = {{1, 0, 0}, {0, 1, 0}, {0, 0, 1}};
Hamil[Hx_, Hy_, Hz_] :=
  ( g μB (Hx Sx + Hy Sy + Hz Sz) + δ (Sz.Sz - 1/3 S (S + 1) I1) +
    ε (Sx.Sx - Sy.Sy) ) /. S -> 1;

```

Matrix element in the general case

Hamil[Hx, Hy, Hz] // Simplify

$$\left\{ \left\{ \frac{\delta}{3} + g \text{Hz} \mu\text{B}, \frac{g (\text{Hx} - i \text{Hy}) \mu\text{B}}{\sqrt{2}}, \epsilon \right\}, \right. \\ \left. \left\{ \frac{g (\text{Hx} + i \text{Hy}) \mu\text{B}}{\sqrt{2}}, -\frac{2\delta}{3}, \frac{g (\text{Hx} - i \text{Hy}) \mu\text{B}}{\sqrt{2}} \right\}, \right. \\ \left. \left\{ \epsilon, \frac{g (\text{Hx} + i \text{Hy}) \mu\text{B}}{\sqrt{2}}, \frac{1}{3} (\delta - 3 g \text{Hz} \mu\text{B}) \right\} \right\}$$

Eigenvalue problems: eugenvalues and eigenfunctions; Hx

eqx1 = Eigensystem[Hamil[Hx, 0, 0]] // Simplify

$$\left\{ \left\{ \frac{1}{3} (\delta - 3\epsilon), \frac{1}{6} \left(-\delta + 3\epsilon - 3 \sqrt{\delta^2 + 2\delta\epsilon + \epsilon^2 + 4g^2 \text{Hx}^2 \mu\text{B}^2} \right), \right. \right. \\ \left. \left. \frac{1}{6} \left(-\delta + 3 \left(\epsilon + \sqrt{\delta^2 + 2\delta\epsilon + \epsilon^2 + 4g^2 \text{Hx}^2 \mu\text{B}^2} \right) \right) \right\}, \right. \\ \left. \{-1, 0, 1\}, \right. \\ \left. \left\{ 1, - \left(g \text{Hx} \mu\text{B} \left(\delta - 3\epsilon + \sqrt{\delta^2 + 2\delta\epsilon + \epsilon^2 + 4g^2 \text{Hx}^2 \mu\text{B}^2} \right) \right) / \right. \right. \\ \left. \left(\sqrt{2} \left(\delta\epsilon + \epsilon^2 + g^2 \text{Hx}^2 \mu\text{B}^2 - \right. \right. \right. \\ \left. \left. \left. \epsilon \sqrt{\delta^2 + 2\delta\epsilon + \epsilon^2 + 4g^2 \text{Hx}^2 \mu\text{B}^2} \right) \right), 1 \right\}, \right. \\ \left. \left\{ 1, \left(g \text{Hx} \mu\text{B} \left(-\delta + 3\epsilon + \sqrt{\delta^2 + 2\delta\epsilon + \epsilon^2 + 4g^2 \text{Hx}^2 \mu\text{B}^2} \right) \right) / \right. \right. \\ \left. \left(\sqrt{2} \left(\delta\epsilon + \epsilon^2 + g^2 \text{Hx}^2 \mu\text{B}^2 + \right. \right. \right. \\ \left. \left. \left. \epsilon \sqrt{\delta^2 + 2\delta\epsilon + \epsilon^2 + 4g^2 \text{Hx}^2 \mu\text{B}^2} \right) \right), 1 \right\} \right\}$$

Eigenvalue problems: eugenvalues and eigenfunctions; Hy

eqy1 = Eigensystem[Hamil[0, Hy, 0]]

$$\left\{ \left\{ \frac{1}{3} (\delta + 3 \epsilon), \frac{1}{6} \left(-\delta - 3 \epsilon - 3 \sqrt{\delta^2 - 2 \delta \epsilon + \epsilon^2 + 4 g^2 \text{Hy}^2 \mu \text{B}^2} \right), \right. \right. \\ \left. \left. \frac{1}{6} \left(-\delta - 3 \epsilon + 3 \sqrt{\delta^2 - 2 \delta \epsilon + \epsilon^2 + 4 g^2 \text{Hy}^2 \mu \text{B}^2} \right) \right\}, \right. \\ \left. \left\{ \{1, 0, 1\}, \left\{ -1, - \left(- \frac{i g \text{Hy} \epsilon \mu \text{B}}{\sqrt{2}} - 1 / (\sqrt{2}) \right) i g \text{Hy} \mu \text{B} \left(\frac{\delta}{3} + \right. \right. \right. \right. \\ \left. \left. \left. \frac{1}{6} \left(\delta + 3 \epsilon + 3 \sqrt{\delta^2 - 2 \delta \epsilon + \epsilon^2 + 4 g^2 \text{Hy}^2 \mu \text{B}^2} \right) \right) \right) \right\} / \right. \\ \left. \left(- \frac{\delta \epsilon}{2} + \frac{\epsilon^2}{2} + \frac{1}{2} g^2 \text{Hy}^2 \mu \text{B}^2 + \frac{1}{2} \epsilon \sqrt{\delta^2 - 2 \delta \epsilon + \epsilon^2 + 4 g^2 \text{Hy}^2 \mu \text{B}^2} \right), 1 \right\}, \right. \\ \left. \left\{ -1, - \left(- \frac{i g \text{Hy} \epsilon \mu \text{B}}{\sqrt{2}} - 1 / (\sqrt{2}) \right) i g \text{Hy} \mu \text{B} \left(\frac{\delta}{3} + \right. \right. \right. \right. \\ \left. \left. \left. \frac{1}{6} \left(\delta + 3 \epsilon - 3 \sqrt{\delta^2 - 2 \delta \epsilon + \epsilon^2 + 4 g^2 \text{Hy}^2 \mu \text{B}^2} \right) \right) \right) \right\} / \right. \\ \left. \left(- \frac{\delta \epsilon}{2} + \frac{\epsilon^2}{2} + \frac{1}{2} g^2 \text{Hy}^2 \mu \text{B}^2 - \frac{1}{2} \epsilon \sqrt{\delta^2 - 2 \delta \epsilon + \epsilon^2 + 4 g^2 \text{Hy}^2 \mu \text{B}^2} \right), 1 \right\} \right\}$$

Eigenvalue problems: eugenvalues and eigenfunctions; Hz

eqz1 = Eigensystem[Hamil[0, 0, Hz]]

$$\left\{ \left\{ -\frac{2\delta}{3}, \frac{1}{3} \left(\delta - 3\sqrt{\epsilon^2 + g^2 Hz^2 \mu B^2} \right), \right. \right. \\ \left. \left. \frac{1}{3} \left(\delta + 3\sqrt{\epsilon^2 + g^2 Hz^2 \mu B^2} \right) \right\}, \right. \\ \left. \left\{ \{0, 1, 0\}, \left\{ -\frac{-g Hz \mu B + \sqrt{\epsilon^2 + g^2 Hz^2 \mu B^2}}{\epsilon}, 0, 1 \right\}, \right. \right. \\ \left. \left. \left\{ -\frac{-g Hz \mu B - \sqrt{\epsilon^2 + g^2 Hz^2 \mu B^2}}{\epsilon}, 0, 1 \right\} \right\} \right\}$$

rule1 = {g → 1, μB → 1}

{g → 1, μB → 1}

Magnetic field // z, ϵ/δ vs $\frac{g\mu B Hz}{\delta}$

energyHz = eqz1[[1]] / δ /. {Hz → δ y, ε → δ x} /. rule1 //

Simplify[#, {x > 0, δ > 0}] &

$$\left\{ -\frac{2}{3}, \frac{1}{3} - \sqrt{x^2 + y^2}, \frac{1}{3} + \sqrt{x^2 + y^2} \right\}$$

```

pz[ $\xi$ _] := Plot[Evaluate[energyHz /. x  $\rightarrow$   $\xi$ ],
  {y, 0, 2},
  PlotStyle  $\rightarrow$  Table[{Thick, Hue[0.15`i]},
    {i, 0, 4}], PlotLabel  $\rightarrow$  { $\xi$ },
  AxesLabel  $\rightarrow$  {" $\frac{g\mu_B H_z}{\delta}$ ", "E/ $\delta$ "},
  Background  $\rightarrow$  GrayLevel[0.5]];
ptz = Evaluate[Table[pz[ $\xi$ ], { $\xi$ , 0, 1, 0.2`}]];
Show[GraphicsGrid[Partition[ptz, 2]]]

```

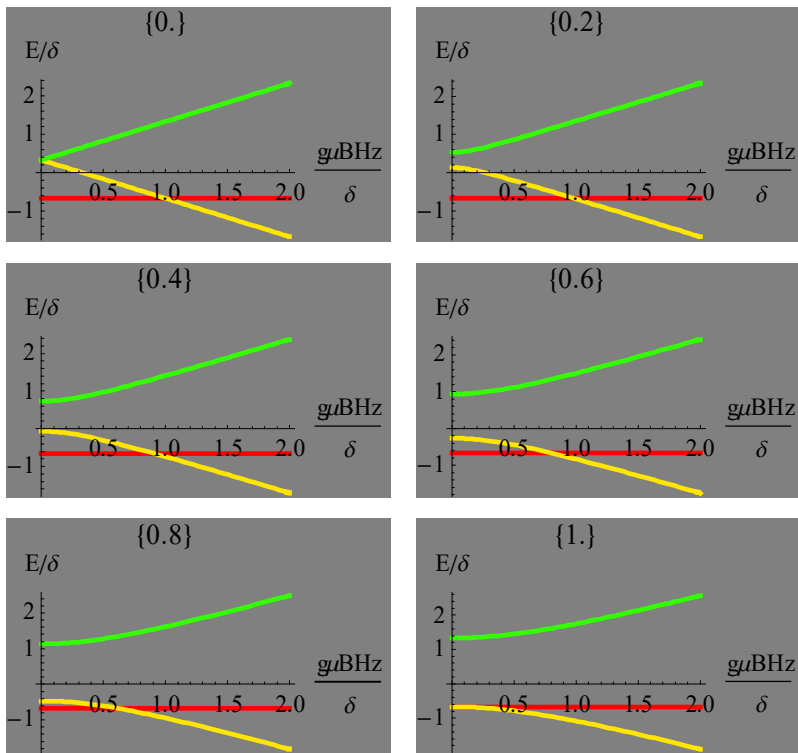


Fig.26 Zeeman splitting of the energy levels for $S = 1$ as a function of $g\mu_B H_z / \delta$. $H//z$. The index shows the value of ε ($= 0 - 1.0$).

Magnetic field //x, E/δ vs $\frac{g\mu_B H x}{\delta}$

```

energyHx =
  eqx1[[1]] /  $\delta$  /. {Hx  $\rightarrow$   $\delta$  y,  $\epsilon$   $\rightarrow$   $\delta$  x} /. rule1 //
  Simplify[#, {x > 0,  $\delta$  > 0}] &
  { $\frac{1}{3} - x$ ,  $\frac{1}{6} \left( -1 + 3x - 3\sqrt{1 + 2x + x^2 + 4y^2} \right)$ ,
   $\frac{1}{6} \left( -1 + 3x + 3\sqrt{1 + 2x + x^2 + 4y^2} \right)$  }

px[ $\xi$ _] := Plot[Evaluate[energyHx /. x  $\rightarrow$   $\xi$ ],
  {y, 0, 2},
  PlotStyle  $\rightarrow$  Table[{Thick, Hue[0.15`i]},
    {i, 0, 4}], PlotLabel  $\rightarrow$  { $\xi$ },
  AxesLabel  $\rightarrow$  { " $\frac{g\mu_B H x \delta}{\delta}$ ", "E/ $\delta$ " },
  Background  $\rightarrow$  GrayLevel[0.5] ];

ptx = Evaluate[Table[px[ $\xi$ ], { $\xi$ , 0, 1, 0.2`}]];
Show[GraphicsGrid[Partition[ptx, 2]]]

```

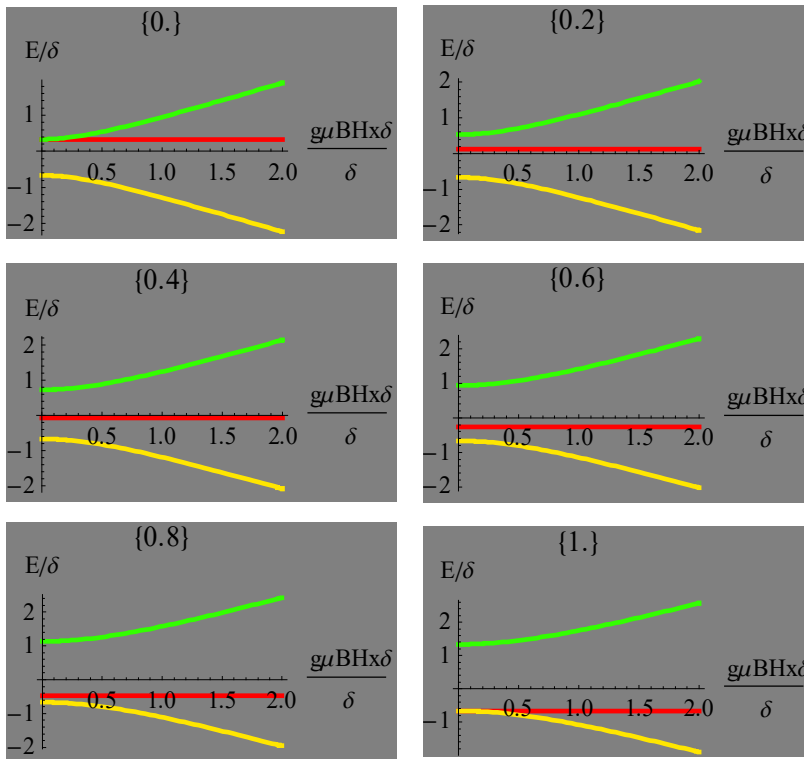


Fig.27 Zeeman splitting of the energy levels for $S=1$ as a function of $g\mu_B H_x / \delta$. H/x . The index shows the value of ε ($= 0 - 1.0$).

Magnetic field // y , ε / δ vs $\frac{g\mu_B H_y}{\delta}$

```

energyHy =
  eqy1[[1]] /  $\delta$  /. {Hy  $\rightarrow$   $\delta$  y,  $\varepsilon \rightarrow \delta$  x} /. rule1 //
  Simplify[#, {x > 0,  $\delta$  > 0}] &

{ $\frac{1}{3} + x$ ,  $\frac{1}{6} \left( -1 - 3x - 3\sqrt{1 - 2x + x^2 + 4y^2} \right)$ ,
  $\frac{1}{6} \left( -1 - 3x + 3\sqrt{1 - 2x + x^2 + 4y^2} \right)$ }

py[ $\xi$ _] := Plot[Evaluate[energyHy /. x  $\rightarrow$   $\xi$ ],
  {y, 0, 2},
  PlotStyle  $\rightarrow$  Table[{Thick, Hue[0.15` i]},
    {i, 0, 4}], PlotLabel  $\rightarrow$  { $\xi$ },
  AxesLabel  $\rightarrow$  {" $\frac{g\mu_B H_y}{\delta}$ ", "E/ $\delta$ "},
  Background  $\rightarrow$  GrayLevel[0.5]];

pty = Evaluate[Table[py[ $\xi$ ], { $\xi$ , 0, 1, 0.2}]];
Show[GraphicsGrid[Partition[pty, 2]]]

```

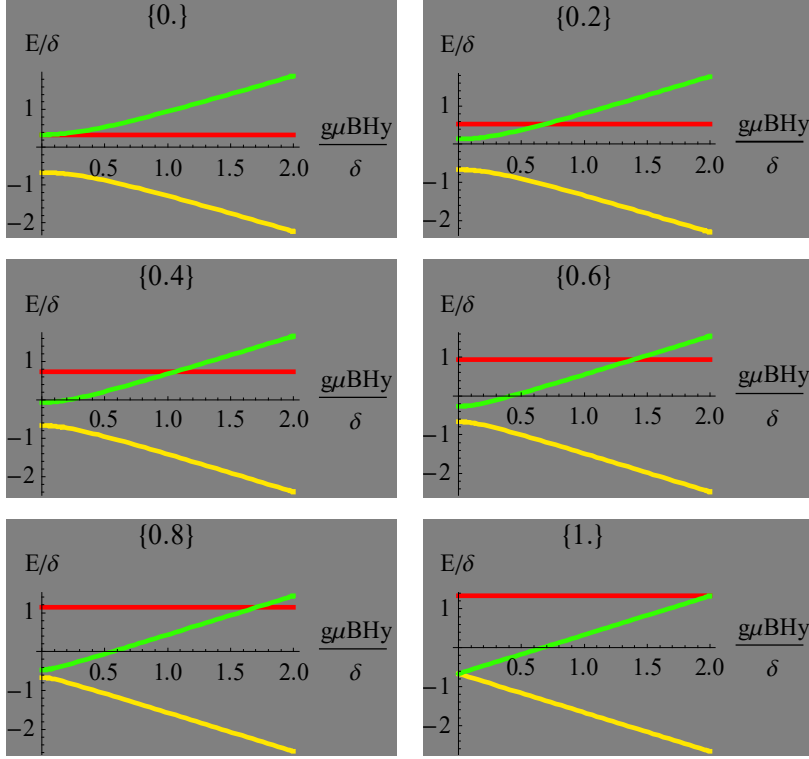


Fig.28 Zeeman splitting of the energy levels for $S = 1$ as a function of $g\mu_B H_x / \delta$. $H//x$. The index shows the value of ε ($= 0 - 1.0$).

12.3 $S = 3/2$

A. Simple case with $\varepsilon = 0$ and $\delta > 0$

For simplicity we consider the spin Hamiltonian with $\varepsilon = 0$ and $\delta > 0$.

$$\hat{H} = \delta \left[\hat{S}_z^2 - \frac{1}{3} S(S+1) \right]. \quad (12.18)$$

Here note that

$$\hat{H} |m_z\rangle = \varepsilon(m_z) |m_z\rangle, \quad (12.19)$$

with

$$\varepsilon(m_z) = \langle m_z | \hat{H} |m_z\rangle = \delta \left(m_z^2 - \frac{5}{4} \right), \quad (12.20)$$

where $|m_z\rangle$ is the eigenket of \hat{S}_z with the eigenvalue $m_z = \pm \frac{3}{2}, \pm \frac{1}{2}$,

$$\hat{S}_z|m_z\rangle = m_z|m_z\rangle, \quad (12.21)$$

For this we get

$$\begin{cases} \varepsilon\left(m_z = \pm\frac{3}{2}\right) = \delta \\ \varepsilon\left(m_z = \pm\frac{1}{2}\right) = -\delta \end{cases} \quad (12.22)$$

Both states are spin doublets (Kramers doublet). This is true for any half-integer spin ($S = 1/2, 3/2, 5/2, \dots$)

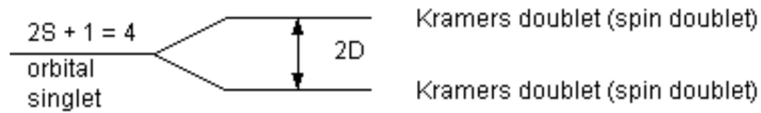


Fig.29 Schematic diagram of the energy levels due to the crystal-field for $S = 3/2$. There are two Kramers doublets.

B. Kramers doublet ((Time reversal operator))

Most operators of interest are either even or odd under the time reversal. $\hat{\Theta}\hat{A}\hat{\Theta}^{-1} = \pm\hat{A}$ (+: even, -: odd).

- (1) $\hat{\Theta}i\hat{\Theta}^{-1} = -i\hat{1}$ (i is a pure imaginary, $\hat{1}$ is the identity operator).
- (2) $\hat{\Theta}\hat{\mathbf{p}}\hat{\Theta}^{-1} = -\hat{\mathbf{p}}$
- (3) $\hat{\Theta}\hat{\mathbf{r}}\hat{\Theta}^{-1} = \hat{\mathbf{r}}$: ($\hat{\Theta}|\mathbf{r}\rangle = |\mathbf{r}\rangle$).
- (4) $\hat{\Theta}\hat{\mathbf{S}}\hat{\Theta}^{-1} = -\hat{\mathbf{S}}$ ($\hat{\mathbf{S}}$ is the spin angular momentum).
- (5) $\hat{\Theta}\hat{H}\hat{\Theta}^{-1} = \hat{H}$, when $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ and $V(\hat{x})$ is a potential energy. The relation is independent of the form of $V(\hat{x})$.

See the Appendix 2 for the detail of the time reversal operator for spin 1/2

((Kramers theorem))

We introduce the time reversal operator $\hat{\Theta}$. Suppose that \hat{H} is invariant under time reversal,

$$[\hat{H}, \hat{\Theta}] = \hat{0}. \quad (12.23)$$

Let $|\phi_n\rangle$ and $\hat{\Theta}|\phi_n\rangle$ be the energy eigenket and its time-reversed states, respectively

$$\hat{H}\hat{\Theta}|\phi_n\rangle = \hat{\Theta}\hat{H}|\phi_n\rangle = \hat{\Theta}E_n|\phi_n\rangle = E_n\hat{\Theta}|\phi_n\rangle. \quad (12.24)$$

$\hat{\Theta}|\phi_n\rangle$ and $|\phi_n\rangle$ belong to the same energy eigenvalue.

When $\hat{\Theta}^2 = -\hat{1}$ (half-integer), $\hat{\Theta}|\phi_n\rangle$ and $|\phi_n\rangle$ are orthogonal.

This means that $\hat{\Theta}|\phi_n\rangle$ and $|\phi_n\rangle$ (having the same energy) must correspond to distinct states (Kramers doublet).

$S = 1$ (even number of electrons) singlet
 $S = 3/2$ (odd number of electrons) doublet (Kramers doublet)

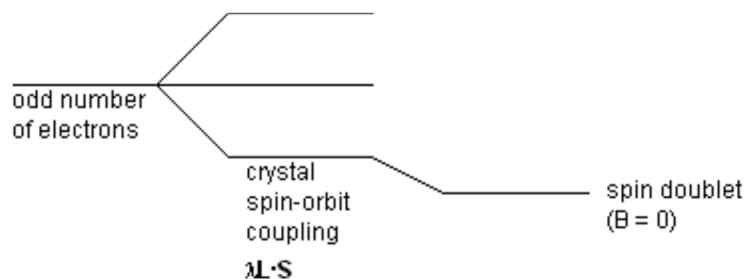


Fig.30 Schematic diagram of the energy levels for the odd number of electrons under the crystal field and spin-orbit interaction. The ground state is a Kramers doublet.

For the odd number of electrons in the incomplete shell, there remains the levels with double degeneracy in the absence of B in spite of any crystal field (Kramers doublet).
 ((Note))

$\text{Co}^{2+}: (3d)^7 \quad n = 7 \quad \text{odd number} \Rightarrow \text{Kramers doublet}$
 $\text{Ni}^{2+}: (3d)^8 \quad n = 8 \quad \text{even number} \Rightarrow \text{No Kramers doublet}$

C. ((Mathematica program)) Energy diagram of the spin Hamiltonian with $S = 3/2$ in the presence of magnetic field

As an example of the application of the spin Hamiltonian, we consider a spin $S = 3/2$ in an axially symmetric system with an external magnetic field $\mathbf{H} = (H_x, H_y, H_z)$.

The energy level of the spin Hamiltonian with $S = 3/2$

$$H = g\mu_B (H_x S_x + H_y S_y + H_z S_z) + \delta [S_z^2 - S(S+1)/3] + \epsilon (S_x^2 - S_y^2)$$

$$J_x[l_, n_, m_] := \frac{1}{2} \sqrt{(l-m)(l+m+1)} \text{KroneckerDelta}[n, m+1] +$$

$$\frac{1}{2} \sqrt{(l+m)(l-m+1)} \text{KroneckerDelta}[n, m-1];$$

$$J_y[l_, n_, m_] :=$$

$$-\frac{1}{2} i \sqrt{(l-m)(l+m+1)} \text{KroneckerDelta}[n, m+1] +$$

$$\frac{1}{2} i \sqrt{(l+m)(l-m+1)} \text{KroneckerDelta}[n, m-1];$$

$$J_z[l_, n_, m_] := m \text{KroneckerDelta}[n, m]$$

$$S_x = \text{Table}[J_x[3/2, n, m], \{n, 3/2, -3/2, -1\},$$

$$\{m, 3/2, -3/2, -1\}];$$

$$S_y = \text{Table}[J_y[3/2, n, m], \{n, 3/2, -3/2, -1\},$$

$$\{m, 3/2, -3/2, -1\}];$$

$$S_z = \text{Table}[J_z[3/2, n, m], \{n, 3/2, -3/2, -1\},$$

$$\{m, 3/2, -3/2, -1\}];$$

$$I1 = \{\{1, 0, 0, 0\}, \{0, 1, 0, 0\}, \{0, 0, 1, 0\}, \{0, 0, 0, 1\}\};$$

$$\text{Hamil}[Hx_, Hy_, Hz_] :=$$

$$\left(g \mu_B (H_x S_x + H_y S_y + H_z S_z) + \delta \left(S_z \cdot S_z - \frac{1}{3} S(S+1) I1 \right) + \right.$$

$$\left. \epsilon (S_x \cdot S_x - S_y \cdot S_y) \right) /. S \rightarrow 3/2;$$

Matrix element in the general case

Hamil[Hx, Hy, Hz] // Simplify

$$\left\{ \left\{ \delta + \frac{3 g \text{Hz} \mu\text{B}}{2}, \frac{1}{2} \sqrt{3} g (\text{Hx} - i \text{Hy}) \mu\text{B}, \sqrt{3} \epsilon, 0 \right\}, \right. \\ \left. \left\{ \frac{1}{2} \sqrt{3} g (\text{Hx} + i \text{Hy}) \mu\text{B}, -\delta + \frac{g \text{Hz} \mu\text{B}}{2}, g (\text{Hx} - i \text{Hy}) \mu\text{B}, \sqrt{3} \epsilon \right\}, \right. \\ \left. \left\{ \sqrt{3} \epsilon, g (\text{Hx} + i \text{Hy}) \mu\text{B}, -\delta - \frac{g \text{Hz} \mu\text{B}}{2}, \frac{1}{2} \sqrt{3} g (\text{Hx} - i \text{Hy}) \mu\text{B} \right\}, \right. \\ \left. \left\{ 0, \sqrt{3} \epsilon, \frac{1}{2} \sqrt{3} g (\text{Hx} + i \text{Hy}) \mu\text{B}, \delta - \frac{3 g \text{Hz} \mu\text{B}}{2} \right\} \right\}$$

Eigenvalue problems: eugenvalues and eigenfunctions for H = Hx, Hy, and Hz

eqx1 = Eigensystem[Hamil[Hx, 0, 0]] // Simplify;

eqy1 = Eigensystem[Hamil[0, Hy, 0]] // Simplify;

eqz1 = Eigensystem[Hamil[0, 0, Hz]] // Simplify;

rule1 = {g → 1, μB → 1};

Magnetic field // z, ϵ/δ vs $\frac{g\mu\text{BHz}}{\delta}$

**energyHz = eqz1[[1]] / δ /. {Hz → δ y, ε → δ x} /. rule1 //
Simplify[#, {x > 0, δ > 0}] &;**

**pz[ξ_] := Plot[Evaluate[energyHz /. x → ξ], {y, 0, 2},
PlotStyle → Table[{Hue[0.15 i], Thick}, {i, 0, 4}],
PlotLabel → {ξ}, PlotPoints → 100,
AxesLabel → {" $\frac{g\mu\text{BHz}}{\delta}$ ", "E/δ"}, Background → GrayLevel[0.5]];**

ptz = Evaluate[Table[pz[ξ], {ξ, 0, 1, 0.2}]];

Show[GraphicsGrid[Partition[ptz, 2]]]

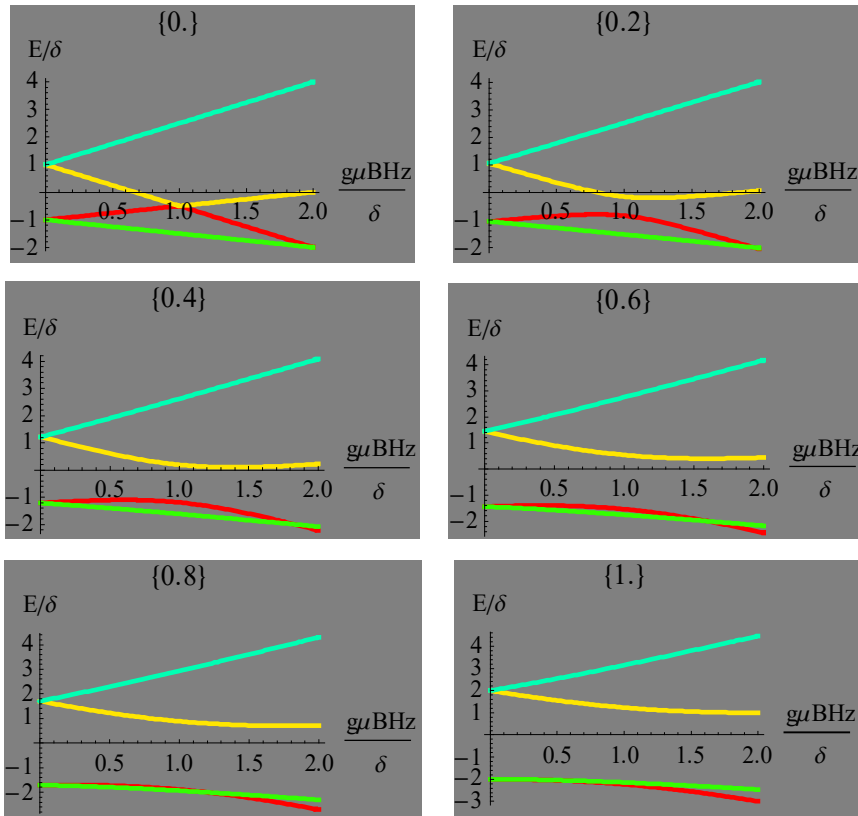


Fig.31 Zeeman splitting of the energy levels for $S = 3/2$ as a function of $g\mu_B H_z / \delta \cdot \mathbf{H} // z$. The index shows the value of $\varepsilon (= 0 - 1.0)$.

Magnetic field //x, E/δ vs $\frac{g\mu_B H_x}{\delta}$

```

energyHx = eqx1[[1]] / δ /. {Hx → δ y, ε → δ x} /. rule1 //
Simplify[#, {x > 0, δ > 0}] &;

px[ξ_] := Plot[Evaluate[energyHx /. x → ξ], {y, 0, 2},
PlotStyle → Table[{Thick, Hue[0.15 i]}, {i, 0, 4}],
PlotLabel → {ξ}, PlotPoints → 100,
AxesLabel → {" $\frac{g\mu_B H_x}{\delta}$ ", "E/δ"}, Background → GrayLevel[0.5]];

ptx = Evaluate[Table[px[ξ], {ξ, 0, 1, 0.2}]];
Show[GraphicsGrid[Partition[ptx, 2]]]

```

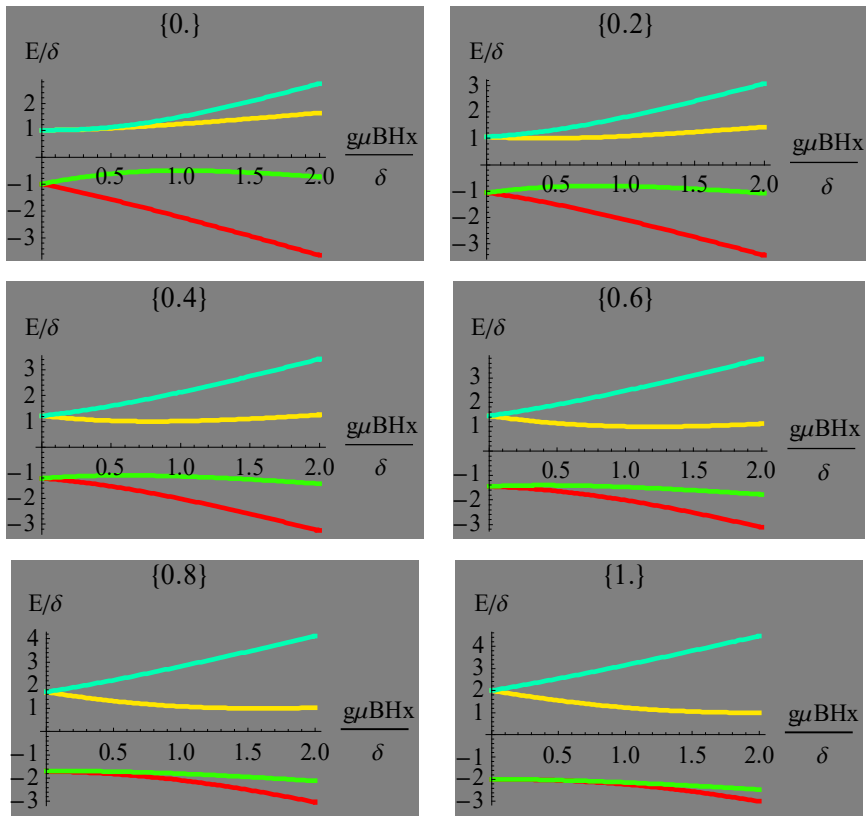


Fig.32 Zeeman splitting of the energy levels for $S = 3/2$ as a function of $g\mu_B H_x / \delta \cdot \mathbf{H} // x$. The index shows the value of $\varepsilon (= 0 - 1.0)$.

Magnetic field // y, E/δ vs $\frac{g\mu_B H_y}{\delta}$

```

energyHy = eqyl[[1]] / δ /. {Hy → δ y, ε → δ x} /. rule1 //
Simplify[#, {x > 0, δ > 0}] &;

py[ε_] := Plot[Evaluate[energyHy /. x → ε], {y, 0, 2},
PlotStyle → Table[{Hue[0.15 i], Thick}, {i, 0, 4}],
Prolog → AbsoluteThickness[2.5], PlotLabel → {ε},
PlotPoints → 100, AxesLabel → {" $\frac{g\mu_B H_y}{\delta}$ ", "E/δ"},
Background → GrayLevel[0.5]];

pty = Evaluate[Table[py[ε], {ε, 0, 1, 0.2}]];
Show[GraphicsGrid[Partition[pty, 2]]]

```

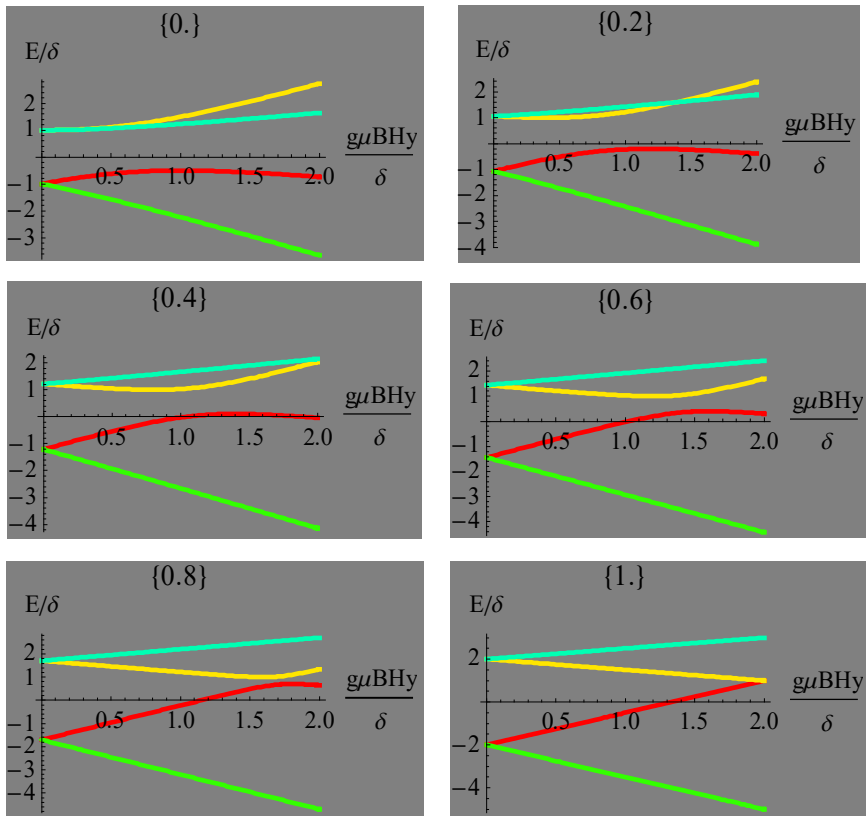



Fig.33 Zeeman splitting of the energy levels for $S = 3/2$ as a function of $g\mu_B H_y / \delta \cdot \mathbf{H} // y$. The index shows the value of ε ($= 0 - 1.0$).

12.4. Energy diagram for $S = 2$

The energy level of the spin Hamiltonian with $S = 2$
 $H = g\mu_B (H_x S_x + H_y S_y + H_z S_z) + \delta [S_z^2 - S(S+1)/3] + \epsilon (S_x^2 - S_y^2)$

```

Jx[l_, n_, m_] :=
  1/2 Sqrt[(l - m) (l + m + 1)] KroneckerDelta[n, m + 1] +
  1/2 Sqrt[(l + m) (l - m + 1)] KroneckerDelta[n, m - 1];
Jy[l_, n_, m_] :=
  -1/2 I Sqrt[(l - m) (l + m + 1)] KroneckerDelta[n, m + 1] +
  1/2 I Sqrt[(l + m) (l - m + 1)] KroneckerDelta[n, m - 1];
Jz[l_, n_, m_] := m KroneckerDelta[n, m]

Sx = Table[Jx[2, n, m], {n, 2, -2, -1}, {m, 2, -2, -1}];
Sy = Table[Jy[2, n, m], {n, 2, -2, -1}, {m, 2, -2, -1}];
Sz = Table[Jz[2, n, m], {n, 2, -2, -1}, {m, 2, -2, -1}];
I1 = {{1, 0, 0, 0, 0}, {0, 1, 0, 0, 0}, {0, 0, 1, 0, 0},
      {0, 0, 0, 1, 0}, {0, 0, 0, 0, 1}};
Hamil[Hx_, Hy_, Hz_] :=
  (g muB (Hx Sx + Hy Sy + Hz Sz) + delta (Sz.Sz - 1/3 S (S + 1) I1) +
   epsilon (Sx.Sx - Sy.Sy)) /. S -> 2;

```

Matrix element for H=0

Hamil[0, 0, 0] // Simplify

$$\begin{aligned} & \{ \{ 2 \delta, 0, \sqrt{6} \epsilon, 0, 0 \}, \\ & \{ 0, -\delta, 0, 3 \epsilon, 0 \}, \{ \sqrt{6} \epsilon, 0, -2 \delta, 0, \sqrt{6} \epsilon \}, \\ & \{ 0, 3 \epsilon, 0, -\delta, 0 \}, \{ 0, 0, \sqrt{6} \epsilon, 0, 2 \delta \} \} \end{aligned}$$

Eigenvalue problems: eugenvalues and eigenfunctions for H = 0

eq1 = Eigensystem[Hamil[0, 0, 0]] // Simplify

$$\begin{aligned} & \{ \{ 2 \delta, -\delta - 3 \epsilon, -\delta + 3 \epsilon, -2 \sqrt{\delta^2 + 3 \epsilon^2}, 2 \sqrt{\delta^2 + 3 \epsilon^2} \}, \\ & \{ \{-1, 0, 0, 0, 1\}, \{0, -1, 0, 1, 0\}, \\ & \{0, 1, 0, 1, 0\}, \{1, 0, -\frac{\sqrt{\frac{2}{3}} (\delta + \sqrt{\delta^2 + 3 \epsilon^2})}{\epsilon}, 0, 1\}, \\ & \{1, 0, \frac{\sqrt{\frac{2}{3}} (-\delta + \sqrt{\delta^2 + 3 \epsilon^2})}{\epsilon}, 0, 1\} \} \} \end{aligned}$$

```

energy = eq1[[1]] /  $\delta$  /. { $\epsilon \rightarrow \delta x$ } //
Simplify[#, { $x > 0$ ,  $\delta > 0$ }] &

{2, -1 - 3 x, -1 + 3 x, -2  $\sqrt{1 + 3 x^2}$ , 2  $\sqrt{1 + 3 x^2}$ }

Plot[Evaluate[energy], {x, -2, 2},
PlotStyle  $\rightarrow$  Table[{Thick, Hue[0.15 i]}, {i, 0, 4}],
Prolog  $\rightarrow$  AbsoluteThickness[2.5],
AxesLabel  $\rightarrow$  {" $\frac{\epsilon}{\delta}$ ", "E/ $\delta$ "}, Background  $\rightarrow$  GrayLevel[0.7]]

```

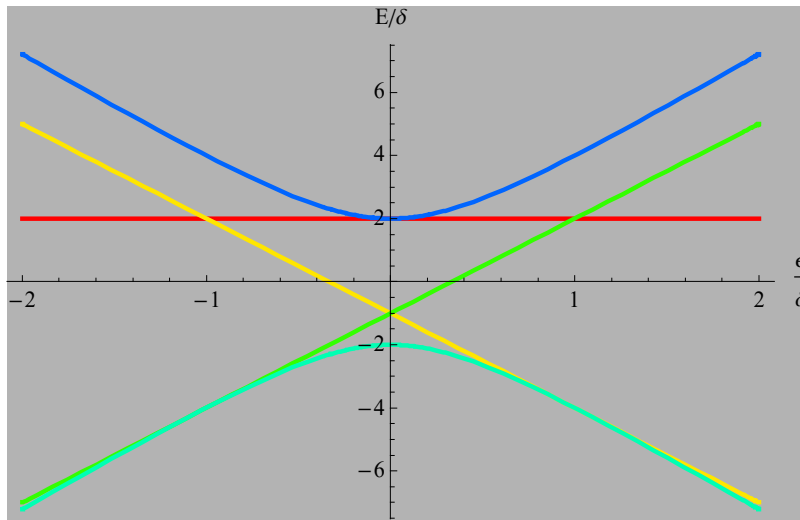


Fig.34 Energy diagram for $S = 2$. E/δ vs ϵ/δ . The ground state is a spin singlet.

12.5. $S = 5/2$

A. Simple case for $S = 5/2$

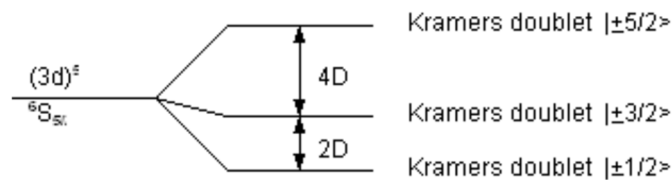


Fig.35 Schematic diagram of the energy levels for $S = 5/2$ under the crystal field. There are three Kramer's doublets.

$(2S + 1) = 6$ degeneracy

$$\hat{H} = D[\hat{S}_z^2 - \frac{1}{3}S(S+1)]. \quad (12.25)$$

Here note that

$$\hat{H}|m_z\rangle = \varepsilon(m_z)|m_z\rangle. \quad (12.26)$$

$$\varepsilon(m_z) = \langle m_z | \hat{H} | m_z \rangle = D(m_z^2 - \frac{1}{3} \cdot \frac{5}{2} \cdot \frac{7}{2}) \quad (12.27)$$

where $m_z = 5/2, 3/2, -1/2, -3/2, -5/2$.

From this we get

$$\varepsilon\left(m_z = \pm \frac{5}{2}\right) = \delta\left(\frac{25}{4} - \frac{35}{12}\right) = \frac{10}{3}\delta$$

$$\varepsilon\left(m_z = \pm \frac{3}{2}\right) = \delta\left(\frac{9}{4} - \frac{35}{12}\right) = -\frac{2}{3}\delta$$

$$\varepsilon\left(m_z = \pm \frac{1}{2}\right) = \delta\left(\frac{1}{4} - \frac{35}{12}\right) = -\frac{8}{3}\delta$$

B. Mathematica for $S = 5/2$ (general case)

The energy level of the spin Hamiltonian with $S = 5/2$
 $H = g\mu_B (H_x S_x + H_y S_y + H_z S_z) + \delta [S_z^2 - S(S+1)/3] + \epsilon (S_x^2 - S_y^2)$

```

Clear["Global`"];
Jx[l_, n_, m_] :=
  1/2 Sqrt[(l - m) (l + m + 1)] KroneckerDelta[n, m + 1] +
  1/2 Sqrt[(l + m) (l - m + 1)] KroneckerDelta[n, m - 1];
Jy[l_, n_, m_] :=
  -1/2 I Sqrt[(l - m) (l + m + 1)] KroneckerDelta[n, m + 1] +
  1/2 I Sqrt[(l + m) (l - m + 1)] KroneckerDelta[n, m - 1];
Jz[l_, n_, m_] := m KroneckerDelta[n, m]

```

```

Sx = Table[Jx[5/2, n, m], {n, 5/2, -5/2, -1},
  {m, 5/2, -5/2, -1}];
Sy = Table[Jy[5/2, n, m], {n, 5/2, -5/2, -1},
  {m, 5/2, -5/2, -1}];
Sz = Table[Jz[5/2, n, m], {n, 5/2, -5/2, -1},
  {m, 5/2, -5/2, -1}];
I1 = {{1, 0, 0, 0, 0, 0}, {0, 1, 0, 0, 0, 0},
  {0, 0, 1, 0, 0, 0}, {0, 0, 0, 1, 0, 0}, {0, 0, 0, 0, 1, 0},
  {0, 0, 0, 0, 0, 1}};
Hamil[Hx_, Hy_, Hz_] :=
  (g μB (Hx Sx + Hy Sy + Hz Sz) + δ (Sz.Sz - 1/3 S (S + 1) I1) +
    ε (Sx.Sx - Sy.Sy)) /. S → 5/2;

```

Matrix element for H=0

```

eq1 = Hamil[0, 0, 0]
      / δ /. {ε → δ x} //
  Simplify[#, {x > 0, δ > 0}] &
  {{10/3, 0, √10 x, 0, 0, 0},
  {0, -2/3, 0, 3√2 x, 0, 0}, {√10 x, 0, -8/3, 0, 3√2 x, 0},
  {0, 3√2 x, 0, -8/3, 0, √10 x},
  {0, 0, 3√2 x, 0, -2/3, 0}, {0, 0, 0, √10 x, 0, 10/3}}

```

Eigenvalue problems: eugenvalues and eigenfunctions for $H = 0$

```
eq1 = Eigenvalues[eq1] // Simplify;  
Plot[Evaluate[eq1], {x, -2, 2},  
PlotStyle -> Table[{Thick, Hue[0.15 i]}, {i, 0, 4}],  
PlotPoints -> 100, AxesLabel -> {" $\frac{\epsilon}{\delta}$ ", " $E/\delta$ "},  
Background -> GrayLevel[0.5]]
```

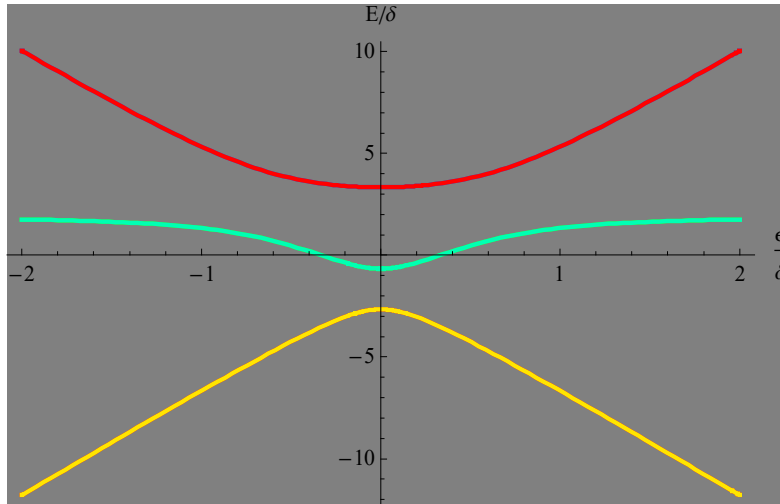


Fig.36 Energy diagram for $S = 5/2$. E/δ vs ϵ/δ . All the three states are a Kramer's doublet.

13. Spin Hamiltonian of Fe^{2+} and Co^{2+} in the trigonal crystal field

13.1. Fe^{2+}

A. Energy diagram

For Fe^{2+} $[(3d)^6]$, the ground state is the orbital triplet. Thus we cannot use the method proposed by Pryce. In this case, we need to determine the energy diagram by taking both the crystal field and the spin orbit interaction into account.¹⁸

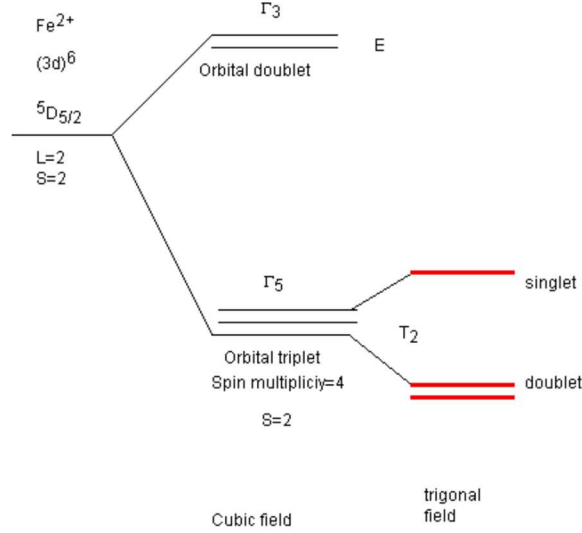


Fig.37 Crystal field splitting of Fe²⁺ ion ground states.

The free-ion (3d)⁶, ⁵D state ($L = 2$, $S = 2$) of the Fe²⁺ is split by the cubic crystal field into the orbital doublet (E) and orbital triplet (T_2), the latter being the lowest one. The orbital wavefunction of the ground orbital triplet are represented by

$$\begin{aligned}
 |-1\rangle &= |\psi_{d1}\rangle = \sqrt{\frac{2}{3}}|\phi_{-2}\rangle + \frac{1}{\sqrt{3}}|\phi_1\rangle \\
 |0\rangle &= |\psi_s\rangle = |\phi_0\rangle \\
 |1\rangle &= |\psi_{d2}\rangle = \sqrt{\frac{2}{3}}|\phi_2\rangle - \frac{1}{\sqrt{3}}|\phi_{-1}\rangle
 \end{aligned} \tag{13.1}$$

where we use the notation, $|l = 3, m\rangle = |\phi_m\rangle$ and we have the relation $\hat{L}_z|\phi_m\rangle = m|\phi_m\rangle$ ($m = -3, -2, -1, 0, 1, 2, 3$). Hereafter we do not use the operators in quantum mechanics for convenience. We consider the splitting of the orbital triplet by the perturbing Hamiltonian given by

$$H_0 = -k\lambda\vec{l} \cdot \vec{S} - \delta(l_z^2 - \frac{2}{3}). \tag{13.2}$$

where k (≈ 1) is a constant, λ ($= -100 \text{ cm}^{-1}$ for Fe²⁺) is a spin-orbit coupling constant, and \mathbf{S} is the spin angular momentum of the magnitude 2. The second term is the tetragonal field. A fictitious angular momentum \mathbf{l} of the magnitude 1 represents the triplet state (\mathbf{l} is antiparallel to the real orbital angular momentum \mathbf{L} ($= -k\mathbf{l}$)).

Since $l_z + S_z$ is a constant of the motion, its eigenvalue m can be used to classify the various states, where $m = l_z' + S_z'$, $l_z|l_z'\rangle = l_z'|l_z'\rangle$ ($l_z' = 1, 0, -1$), and $S_z|S_z'\rangle = S_z'|S_z'\rangle$ ($S_z' = 2, 1, 0, -1, -2$). There are 15 states. A notation $|l_z', S_z'\rangle$ is used to specify these states.

$m = l_z' + S_z'$,	Eigenfunctions
3	$ l_z'=1, S_z'=2\rangle$
2	$ 1,1\rangle, 0,2\rangle$
1	$ 1,0\rangle, 0,1\rangle, -1,2\rangle$
0	$ 1,-1\rangle, 0,0\rangle, -1,1\rangle$
-1	$ 1,-2\rangle, 0,-1\rangle, -1,0\rangle$
-2	$ 0,-2\rangle, -1,-1\rangle$
-3	$ -1,-2\rangle$

We have the splitting of the ground orbital triplet by the spin-orbit coupling λ' and the trigonal field $\delta (>0)$. The energy levels are denoted by

$$E_3 (m = \pm 3), E_2^{(\pm)} (m = \pm 2), E_1^{(i)} (i = 1, 2, 3) (m = \pm 1), E_0^{(0)} \text{ and } E_0^{(\pm)} (m = 0).$$

Here we use $x = \frac{\delta}{\lambda'}$.

(i) $m = \pm 3 (E_3)$

$$\frac{E_3}{\lambda'} = -\frac{x}{3} - 2$$

(ii) $m = \pm 2 [E_2]$

$$\frac{E_2}{\lambda'} = \frac{x}{6} - \frac{1}{2} \pm \frac{1}{2} \sqrt{9 + 2x + x^2}$$

(iii) $m = \pm 1 [E_1^{(1)}, E_1^{(2)}, E_1^{(3)}]$

$$\frac{E_1^{(i)}}{\lambda'} = -\frac{x}{3} + 1 + \xi_i \quad (i = 1, 2, 3).$$

where

$$x = \xi_i + 1 - \frac{3}{\xi_i + 1} - \frac{2}{\xi_i - 1}$$

(iv) $m = 0 [E_0^{(0)}, E_0^{(\pm)}]$

$$\frac{E_0^{(0)}}{\lambda'} = -\frac{x}{3} + 1, \quad \left(\frac{E_0^{(\pm)}}{\lambda'} + \frac{x}{3} - 1\right)\left(\frac{E_0^{(\pm)}}{\lambda'} - \frac{2x}{3}\right) = 6$$

The ground level is either $E_0^{(+)}$ or $E_1^{(1)}$, depending on the sign of x . All the energy states except for $E_1^{(1)}$ and $E_0^{(+)}$ might be neglected in the first approximation, since these lowest levels lie 100 cm^{-1} below the others.

Thus we may use a *fictitious spin* $s = 1$ for the lowest three states denoted by the eigenkets $|\psi_0\rangle$ for the singlet and $|\psi_{\pm 1}\rangle$ for the doublet:

$$|\psi_{\pm 1}\rangle = c_1|\pm 1, 0\rangle + c_2|0, \pm 1\rangle + c_3|\mp 1, \pm 2\rangle, \quad \text{for } E = E_1^{(1)}, \quad (13.3)$$

$$|\psi_0\rangle = a_1|1, -1\rangle + a_2|0, 0\rangle + a_3|-1, 1\rangle \quad \text{for } E = E_0^{(+)}. \quad (13.4)$$

The parameters $c_1, c_2, c_3, a_1, a_2,$ and a_3 are defined by

$$c_1^2 + c_2^2 + c_3^2 = 1, \quad a_1^2 + a_2^2 + a_3^2 = 1, \quad (13.5)$$

$$c_1 = -\frac{\sqrt{3}\alpha}{1 + \xi_1}, \quad c_2 = \alpha, \quad c_3 = \frac{\sqrt{2}\alpha}{1 - \xi_1}, \quad (13.5)$$

$$a_1 = a_3 = -\frac{\sqrt{3}}{\sqrt{\xi_0^2 + 6}}, \quad a_2 = \frac{\xi_0}{\sqrt{\xi_0^2 + 6}}, \quad (13.6)$$

where

$$\alpha^2 = \left[\frac{3}{(1 + \xi_1)^2} + 1 + \frac{2}{(1 - \xi_1)^2} \right]^{-1}, \quad (13.7)$$

and the parameters ξ_0 and ξ_1 are related to the energy $E_1^{(1)}$ and $E_0^{(+)}$ through

$$\frac{E_1^{(1)}}{\lambda'} = -\frac{x}{3} + 1 + \xi_1, \quad \frac{E_0^{(+)}}{\lambda'} = -\frac{x}{3} + 1 + \xi_0. \quad (13.8)$$

B. Spin Hamiltonian with fictitious spin $s = 1$.

The g -factors can be evaluated as $g_c = g_c^{(0)} + \Delta g$ and $g_a = g_a^{(0)} + \Delta g$, where Δg is due to the effect of spin-orbit coupling in admixing the upper orbital levels into the ground three orbitals, and $g_c^{(0)}$ and $g_a^{(0)}$ are given by

$$g_c^{(0)} = \langle \psi_{\pm 1} | V_z | \psi_{\pm 1} \rangle = -kc_1^2 + 2c_2^2 + (k+4)c_3^2, \quad (13.9)$$

$$g_c^{(0)} = \sqrt{2} \langle \psi_0 | V_x | \psi_{\pm 1} \rangle = -k(c_1a_2 + c_2a_3) + 2\sqrt{3}(c_1a_1 + c_2a_2) + 2\sqrt{2}c_3a_3. \quad (13.10)$$

where $V_z = -kl_z + 2S_z$ and $V_x = -kl_x + 2S_x$. For a given k , the two $g_c^{(0)}$ and $g_a^{(0)}$ values are functions of the single parameter x and so they bear a functional relationship to each other. In Fig.40 we show the $g_c^{(0)}$ and $g_a^{(0)}$ as a function of x with k as a parameter: $g_c^{(0)} > g_a^{(0)}$ for $x < 0$ and $g_c^{(0)} < g_a^{(0)}$ for $x > 0$. Note that $x = -1.27$ for FeCl_2 .

If we take the z axis parallel to the c axis, and x, y axes perpendicular to it, we have

$$S_x = qs_x, \quad S_y = qs_y, \quad S_z = ps_z,$$

Here

$$S_z|\psi_0\rangle = -a_1|1,-1\rangle + a_3|-1,1\rangle, \quad S_z|\psi_{\pm 1}\rangle = \pm(c_2|0,\pm 1\rangle + 2c_3|\mp 1,\pm 2\rangle), \quad (13.11)$$

$$\langle\psi_{\pm 1}|S_z|\psi_{\pm 1}\rangle = \pm(c_2^2 + 2c_3^2) = \pm p, \quad \langle\psi_0|S_z|\psi_0\rangle = 0, \quad (13.12)$$

$$\langle\psi_1|S^+|\psi_0\rangle = \sqrt{6}(c_1a_1 + c_2a_2) + 2c_3a_3 = \sqrt{2}q, \quad (13.13)$$

where

$$p = c_2^2 + 2c_3^2, \quad q = \sqrt{3}(c_1a_1 + c_2a_2) + \sqrt{2}c_3a_3. \quad (13.14)$$

((Note))

Note that for $s = 1$, $\langle\psi_1|s^+|\psi_0\rangle = \sqrt{2}$, where $|\psi_0\rangle, |\psi_{\pm 1}\rangle$ are assumed to be eigenkets of $s = 1$. In other words, we have

$$\langle\psi_1|S^+|\psi_0\rangle = \langle\psi_1|qs^+|\psi_0\rangle = \sqrt{2}q = \sqrt{6}(c_1a_1 + c_2a_2) + 2c_3a_3, \quad (13.15)$$

$$\langle\psi_1|S_z|\psi_1\rangle = \langle\psi_1|ps_z|\psi_1\rangle = p = c_2^2 + 2c_3^2. \quad (13.16)$$

If we assume that the exchange interaction within the ground orbital triplet is given by

$$H_{ij} = -2J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j, \quad (13.17)$$

the effective exchange interaction nearest spins within the ground levels is expressed by

$$H_{ij} = -2J_{ij}[q^2(s_{ix}s_{jx} + s_{iy}s_{jy}) + p^2s_{iz}s_{jz}]. \quad (13.19)$$

Thus the exchange interaction becomes anisotropic. This is rewritten as

$$H_{ij} = -2J_{ij}[q^2\mathbf{s}_i \cdot \mathbf{s}_j + (p^2 - q^2)s_{iz}s_{jz}]. \quad (13.20)$$

The resultant spin Hamiltonian for Fe^{2+} is given by

$$H = -D \sum_i (s_{iz}^2 - \frac{2}{3}) - 2J \sum_{\langle i,j \rangle} \mathbf{s}_i \cdot \mathbf{s}_j - 2J_A \sum_{\langle i,j \rangle} s_{iz} s_{jz}, \quad (13.21)$$

where the fictitious spin $s = 1$. $J = q^2 J_{ij}$, $D \approx \delta/10 (>0)$ is the single ion anisotropy, and J_A ($=J(p^2 - q^2)/q^2$) is the anisotropic exchange interaction. The second term is the isotropic exchange interaction, and third term is the anisotropic exchange interaction. The spin anisotropy parameter D_{eff} is defined as $D_{\text{eff}} (= D(s - 1/2) + 2zsJ_A)$. The XY (Ising) symmetry appears when $D_{\text{eff}} < 0$ ($D_{\text{eff}} > 0$).

C. Mathematica-Program: energy diagram of Fe^{2+} in the trigonal field

Here we calculate the energy levels, the probability amplitudes and parameters of spin Hamiltonian of Fe^{2+} ion in the trigonal field.

((Mathematica program))

Fictitious spin $s=1$ in Fe^{2+} , Spin Hamiltonian

```
Clear["Global`"]
E3 = -(- $\frac{x}{3}$  - 2); E2p = -( $\frac{x}{6}$  -  $\frac{1}{2}$  +  $\frac{1}{2} \sqrt{x^2 + 2x + 9}$ );
E2n = -( $\frac{x}{6}$  -  $\frac{1}{2}$  -  $\frac{1}{2} \sqrt{x^2 + 2x + 9}$ );
E13[x1_] := Module[{t, y}, t = x1; eq11 = t == (y + 1) -  $\frac{3}{y+1}$  -  $\frac{2}{y-1}$ ;
s1 = NSolve[eq11, y] // Flatten; E13[t] = -(- $\frac{t}{3}$  + (y + 1)) /. s1[[1]];
E12[x2_] := Module[{t, y}, t = x2; eq22 = t == (y + 1) -  $\frac{3}{y+1}$  -  $\frac{2}{y-1}$ ;
s2 = NSolve[eq22, y] // Flatten; E12[t] = -(- $\frac{t}{3}$  + (y + 1)) /. s2[[2]];
E11[x3_] := Module[{t, y}, t = x3; eq33 = t == (y + 1) -  $\frac{3}{y+1}$  -  $\frac{2}{y-1}$ ;
s3 = NSolve[eq33, y] // Flatten; E11[t] = -(- $\frac{t}{3}$  + (y + 1)) /. s3[[3]];
E0 = -(- $\frac{x}{3}$  + 1);
E0p[x4_] := Module[{t, y}, t = x4; eq44 = (y +  $\frac{t}{3}$  - 1) (y -  $\frac{2t}{3}$ ) - 6 == 0;
s4 = NSolve[eq44, y] // Flatten; E0p[t] = -y /. s4[[2]];
E0n[x5_] := Module[{t, y}, t = x5; eq55 = (y +  $\frac{t}{3}$  - 1) (y -  $\frac{2t}{3}$ ) - 6 == 0;
s5 = NSolve[eq55, y] // Flatten; E0n[t] = -y /. s5[[1]]
```

Wavefunctions, g-values, anisotropic exchange interaction

```

c1[x1_, k1_] := Module[{t, k, y, s1, y1}, t = x1; k = k1;
  eq11 = t == (y + 1) -  $\frac{3}{y+1}$  -  $\frac{2}{y-1}$ ; s1 = NSolve[eq11, y] // Flatten;
  y1 = y /. s1[[3]]; c1[t, k] =  $\frac{1}{\sqrt{\frac{3}{(1+y1)^2} + 1 + \frac{2}{(1-y1)^2}}}$   $\left( \frac{-\sqrt{3}}{1+y1} \right)$ ;
c2[x1_, k1_] := Module[{t, k, y, s1, y1}, t = x1; k = k1;
  eq11 = t == (y + 1) -  $\frac{3}{y+1}$  -  $\frac{2}{y-1}$ ; s1 = NSolve[eq11, y] // Flatten;
  y1 = y /. s1[[3]]; c2[t, k] =  $\frac{1}{\sqrt{\frac{3}{(1+y1)^2} + 1 + \frac{2}{(1-y1)^2}}}$ ];
c3[x1_, k1_] := Module[{t, k, y, s1, y1}, t = x1; k = k1;
  eq11 = t == (y + 1) -  $\frac{3}{y+1}$  -  $\frac{2}{y-1}$ ; s1 = NSolve[eq11, y] // Flatten;
  y1 = y /. s1[[3]]; c3[t, k] =  $\frac{1}{\sqrt{\frac{3}{(1+y1)^2} + 1 + \frac{2}{(1-y1)^2}}}$   $\left( \frac{\sqrt{2}}{1-y1} \right)$ ;
a1[x1_, k1_] := Module[{t, k, z, s2, y0}, t = x1; k = k1;
  eq22 =  $\left( z + \frac{t}{3} - 1 \right) \left( z - \frac{2t}{3} \right) - 6 == 0$ ; s2 = NSolve[eq22, z] // Flatten;
  y0 =  $\left( z + \frac{t}{3} - 1 \right) /. s2[[2]]$ ; a1[t, k] =  $-\frac{\sqrt{3}}{\sqrt{6+y0^2}}$ ;
a2[x1_, k1_] := Module[{t, k, z, s2, y0}, t = x1; k = k1;
  eq22 =  $\left( z + \frac{t}{3} - 1 \right) \left( z - \frac{2t}{3} \right) - 6 == 0$ ; s2 = NSolve[eq22, z] // Flatten;
  y0 =  $\left( z + \frac{t}{3} - 1 \right) /. s2[[2]]$ ; a2[t, k] =  $\frac{y0}{\sqrt{6+y0^2}}$ ;
a3[x1_, k1_] := Module[{t, k, z, s2, y0}, t = x1; k = k1;
  eq22 =  $\left( z + \frac{t}{3} - 1 \right) \left( z - \frac{2t}{3} \right) - 6 == 0$ ; s2 = NSolve[eq22, z] // Flatten;
  y0 =  $\left( z + \frac{t}{3} - 1 \right) /. s2[[2]]$ ; a3[t, k] =  $-\frac{\sqrt{3}}{\sqrt{6+y0^2}}$ ];
q[x_, k_] :=  $\sqrt{3}$  (c1[x, k] a1[x, k] + c2[x, k] a2[x, k]) +
 $\sqrt{2}$  c3[x, k] a3[x, k]; p[x_, k_] := c2[x, k]^2 + 2 c3[x, k]^2;
gc[x_, k_] := -k c1[x, k]^2 + 2 c2[x, k]^2 + (k + 4) c3[x, k]^2;
ga[x_, k_] := -k (c1[x, k] a2[x, k] + c2[x, k] a3[x, k]) +
2  $\sqrt{3}$  (c1[x, k] a1[x, k] + c2[x, k] a2[x, k]) + 2  $\sqrt{2}$  c3[x, k] a3[x, k]

```

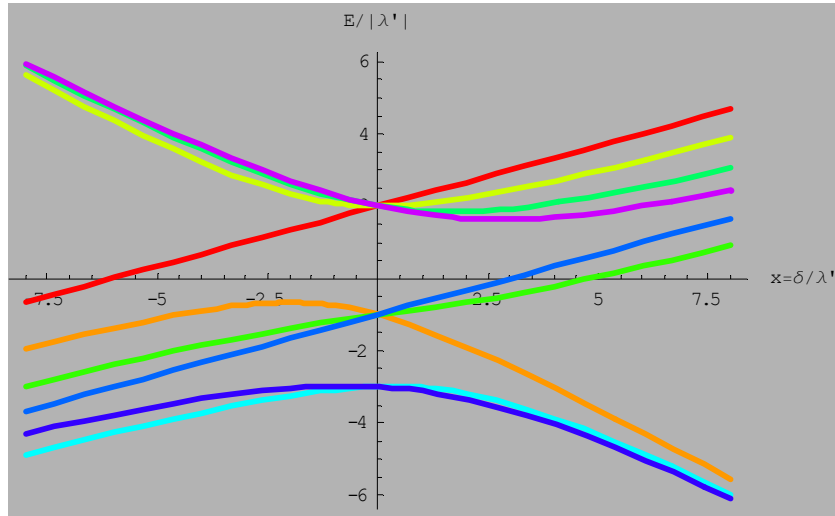
Overview of the Energy levels, E3, E2+, E2-, E13[x], E12[x], E11[x], E0, E0+[x], E0-[x] as a function of x

```

Plot[Evaluate[{E3, E2p, E2n, E13[x], E12[x], E11[x], E0, E0p[x], E0n[x]}, {x, -8, 8}], PlotStyle -> Table[Hue[0.1

```

```
i], {i, 0, 8}], Prolog → AbsoluteThickness [3],
AxesLabel → {"x = δ/λ'", "E/|λ'|"}, Background → GrayLevel [0.7]]
```

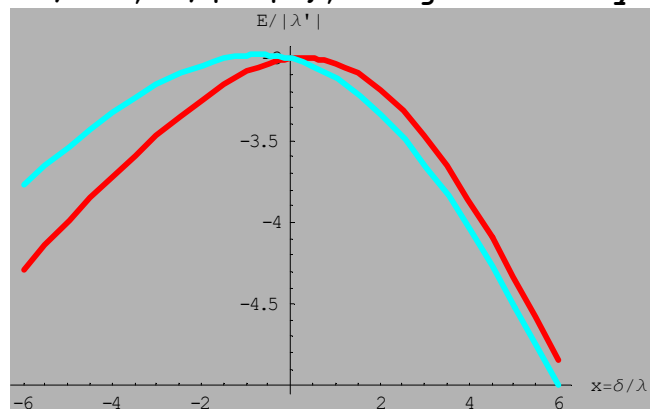


-Graphics-

Fig.38 The splitting of the ground orbital triplet by the spin-orbit coupling and the trigonal field for Fe^{2+} ion in the trigonal field. E_3 (red), $E_2^{(-)}$ (yellow), $E_1^{(3)}$ (green), $E_0^{(-)}$ (purple), $E_0^{(0)}$ (blue), $E_1^{(2)}$ (green), $E_2^{(+)}$ (orange), $E_1^{(1)}$ (light blue), and $E_0^{(+)}$ (blue).

The ground level : either $E_{11}[x]$ or $E_{0+}[x]$ as a function of x

```
Plot[Evaluate[{E11[x], E0p[x]}], {x, -6, 6},
PlotStyle → Table[Hue[0.5
i], {i, 0, 1}], Prolog → AbsoluteThickness [3],
AxesLabel → {"x = δ/λ'", "E/|λ'|"}, Background → GrayLevel [0.7]]
```



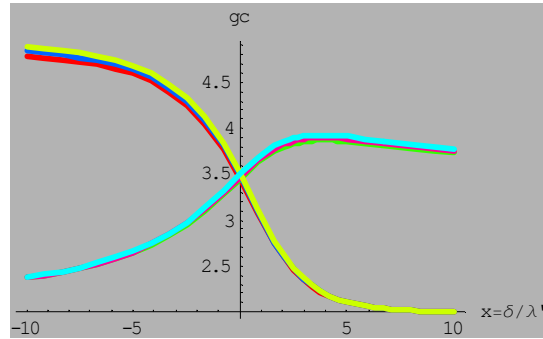
-Graphics-

Fig.39 The detail of the two energy levels $E_1^{(1)}$ (red) and $E_0^{(+)}$ (light blue) as a ground state for Fe^{2+} ion in the trigonal field.

Plot of the g-factors $g_c[x,k]$ and $g_a[x,k]$ as a function of x with $k = 0.9, 0.95, \text{ and } 1.0$

```
Plot[Evaluate[Table[{gc[x,k], ga[x,k]}], {k, 0.9, 1, 0.05}]], {x, -
10, 10}, PlotStyle → Table[Hue[0.3
```

```
i], {i, 0, 10}], Prolog -> AbsoluteThickness[3],
AxesLabel -> {"x = δ/λ'", "gc"}, Background -> GrayLevel[0.7]]
```

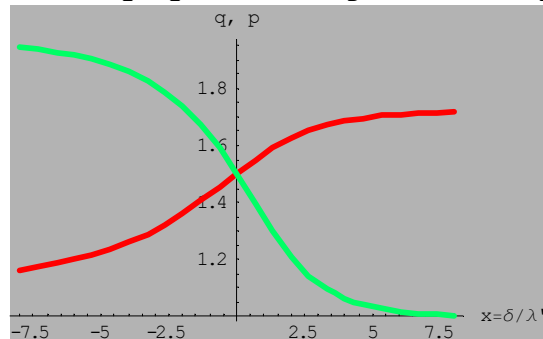


-Graphics-

Fig.40 Plot of g_c (red) and g_a (blue) as a function of x for Fe^{2+} ion in the trigonal field. $k = 0.9, 0.95,$ and $1.$

Anisotropic parameters of spin Hamiltonian q and p , Plot of q and p as a function of x with $k = 0.9, 0.95,$ and 1.0

```
Plot[Evaluate[Table[{q[x,k], p[x,k]}, {k, 0.9, 1.0, 0.5}]], {x, -
8, 8}, PlotStyle -> Table[Hue[0.4
i], {i, 0, 8}], Prolog -> AbsoluteThickness[3],
AxesLabel -> {"x = δ/λ'", "q, p"}, Background -> GrayLevel[0.7]]
```

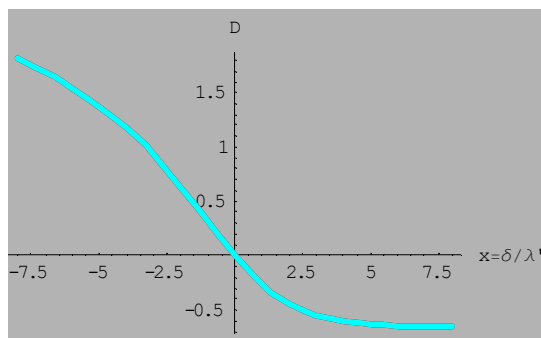


-Graphics-

Fig.41 Plot of the parameters q (red) and p (green) for Fe^{2+} ion in the trigonal field. $k = 0.9, 0.95,$ and $1.$

Plot of $\frac{p^2 - q^2}{q^2}$ as a function of x . $k = 0.8, 0.9, 1, 1.1$

```
Plot[Evaluate[Table[\frac{p[x,k]^2 - q[x,k]^2}{q[x,k]^2}, {k, 0.8, 1.1, 0.1}]],
{x, -8, 8}, PlotStyle -> Table[Hue[0.5 i], {i, 0, 8}],
Prolog -> AbsoluteThickness[3], AxesLabel -> {"x = δ/λ'", "D"},
Background -> GrayLevel[0.7]]
```

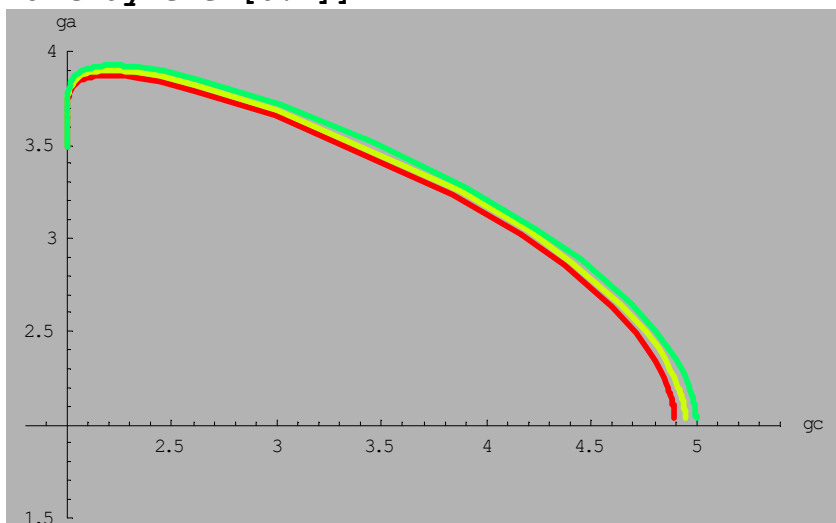


-Graphics-

Fig.42 Plot of the spin anisotropy parameter $p^2/q^2 - 1$ as a function of x for Fe^{2+} ion in the trigonal field. $k = 0.8, 0.9, 1, \text{ and } 1.1$.

gc vs ga curves with k = 0.9, 0.95, 1.0

```
ParametricPlot[Evaluate[Table[{gc[x,k],ga[x,k]},{k,0.9,1.0,0.05}]],{x,-100,100},
PlotPoints->100,PlotStyle->Table[Hue[0.2i],{i,0,10}],Prolog->AbsoluteThickness[3],
AxesLabel->{"gc","ga"},PlotRange->{{1.8,5.4},{1.5,4}},
Background->GrayLevel[0.7]]
```

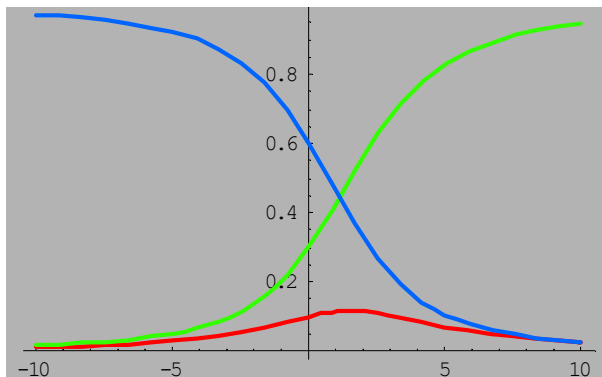


-Graphics-

Fig.43 Calculated relation between g_c and g_a -values of Fe^{2+} ion in the trigonal field. $k = 0.9$ (red), 0.95 (yellow), and 1.0 (green).

squares of amplitudes (c1, c2, c3) of the wave functions as a function of x k = 0.9

```
Plot[Evaluate[{c1[x,0.9]^2,c2[x,0.9]^2,c3[x,0.9]^2}],{x,-10,10},
PlotStyle->Table[Hue[0.3i],{i,0,3}],Prolog->AbsoluteThickness[2],
Background->GrayLevel[0.7]]
```

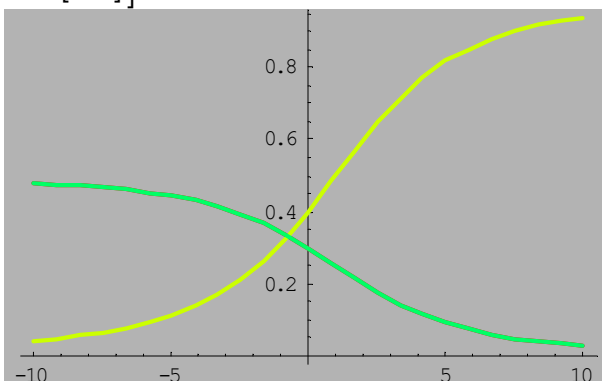



-Graphics-

Fig.44 Plot of the probability amplitudes c_1^2 (red), c_2^2 (blue), and c_3^2 (green), as a function of x for Fe^{2+} ion in the trigonal field. $k = 0.9$

Squares of amplitudes (a_1, a_2, a_3) of the wave functions, as a function of x
 $k = 0.9$

```
Plot[Evaluate[{a1[x, 0.9]^2, a2[x, 0.9]^2, a3[x, 0.9]^2}], {x, -10, 10},
PlotStyle -> Table[Hue[0.2 i], {i, 0, 4}], Prolog -> AbsoluteThickness[2],
Background -> GrayLevel[0.7]
```



-Graphics-

Fig.45 Plot of the probability amplitude a_n^2 ($n = 1 - 3$) for Fe^{2+} ion in the trigonal field. $k = 0.9$.

13.2. Co^{2+}

A. Energy diagram of Co^{2+}

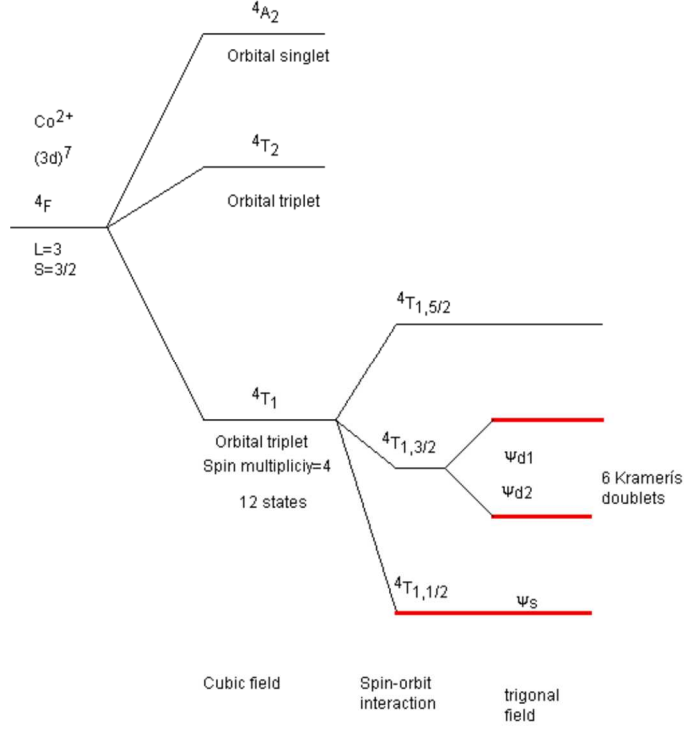


Fig.46 Crystal-field splittings of Co^{2+} ion ground states.

For $Co^{2+} [(3d)^7]$, the ground state is the orbital triplet. Thus we cannot use the method proposed by Pryce. In this case, we need to determine the energy diagram by taking both the crystal field and the spin orbit interaction into account.^{19,20}

In a cubic crystal field the free-ion $3d^7$ ($L = 3, S = 3/2$), $4F$ state is split into two orbital triplets and one orbital singlet with a triplet the lowest,

$$\begin{aligned}
 |-1\rangle = |\psi_{d1}\rangle &= \sqrt{\frac{5}{6}}|\phi_2\rangle + \frac{1}{\sqrt{6}}|\phi_{-1}\rangle \\
 |0\rangle = |\psi_s\rangle &= \frac{2}{3}|\phi_0\rangle - \frac{1}{3}\sqrt{\frac{5}{2}}[|\phi_3\rangle - |\phi_{-3}\rangle], \\
 |1\rangle = |\psi_{d2}\rangle &= \sqrt{\frac{5}{6}}|\phi_{-2}\rangle - \frac{1}{\sqrt{6}}|\phi_1\rangle
 \end{aligned} \tag{13.22}$$

where we use the notation, $|l = 2, m\rangle = |\phi_m\rangle$ and we have the relation $\hat{L}_z|\phi_m\rangle = m|\phi_m\rangle$ ($m = -2, -1, 0, 1, 2$). We can verify that

$$\langle \pm 1 | \hat{L}_z | \pm 1 \rangle = \mp \frac{3}{2}, \quad \langle 0 | \hat{L}_z | 0 \rangle = 0, \quad \langle \pm 1 | \hat{L}_z | 0 \rangle = \langle 0 | \hat{L}_z | \pm 1 \rangle = \langle \pm 1 | \hat{L}_z | \mp 1 \rangle = 0. \tag{13.23}$$

We can show that all the matrix element of $\hat{\mathbf{L}}$ within the states $|0\rangle, |\pm 1\rangle$, are exactly the same as the matrix element of $-3I/2$, where I is a fictitious angular momentum of the magnitude 1. Hereafter we do not use the operators in quantum mechanics for convenience.

Now we consider the splitting of the ground orbital triplet by the tetragonal crystal field together with the spin-orbit coupling,

$$H_0 = -\frac{3}{2}k\lambda\vec{l} \cdot \vec{S} - \delta(l_z^2 - \frac{2}{3}), \quad (13.24)$$

where $\lambda' = k\lambda$, λ is the spin-orbit coupling constant and may be different from its free-ion value of -180 cm^{-1} , and k is the orbital reduction factor due to admixture of $4P$ into $4T_1$ and is less than but of order unity, δ is the trigonal field strength, and S is the spin angular momentum of the magnitude $3/2$. A fictitious angular momentum I of the magnitude 1 represents the triplet state (I is antiparallel to the real orbital angular momentum $L = -3kI/2$).

Since $l_z + S_z$ is a constant of the motion, its eigenvalue m can be used to classify the various states, where $m = l_z' + S_z'$, ($l_z' = 1, 0, -1$ and $S_z' = 3/2, 1/2, -1/2, -3/2$). There are 12 eigenfunctions.

$m = l_z' + S_z'$,	Eigenfunctions
$\frac{5}{2}$	$ l_z' = 1, S_z' = \frac{3}{2}\rangle$
$\frac{3}{2}$	$ 1, \frac{1}{2}\rangle, 0, \frac{3}{2}\rangle$
$\frac{1}{2}$	$ 1, -\frac{1}{2}\rangle, 0, \frac{1}{2}\rangle, -1, \frac{3}{2}\rangle$
$-\frac{1}{2}$	$ -1, \frac{1}{2}\rangle, 0, -\frac{1}{2}\rangle, 1, -\frac{3}{2}\rangle$
$-\frac{3}{2}$	$ -1, -\frac{1}{2}\rangle, 0, -\frac{3}{2}\rangle$
$-\frac{5}{2}$	$ -1, -\frac{3}{2}\rangle$

The secular equation reduces to three separate equations for energy. The energy eigenvalues are as follows.

$$\begin{aligned} E_s(m = \pm 5/2), \\ E_q^{(\pm)}(m = \pm 3/2), \\ E_c^{(0)}, E_c^{(1)}, \text{ and } E_c^{(2)}(m = \pm 1/2). \end{aligned}$$

For all values of x , $E_c^{(0)}$ is the lowest energy. The wave functions $|\psi_{\pm 1}\rangle$, $|\psi_{\pm 3}\rangle$, and $|\psi_{\pm 4}\rangle$ for $m = \pm 1/2$ are given by

$$|\psi_{\pm 1}\rangle = c_1 \left| \mp 1, \pm \frac{3}{2} \right\rangle + c_2 \left| 0, \pm \frac{1}{2} \right\rangle + c_3 \left| \pm 1, \mp \frac{1}{2} \right\rangle \quad \text{for } E_{\pm 1} = E_c^{(0)}, \quad (13.25)$$

$$|\psi_{\pm 3}\rangle = c_4 \left| \mp 1, \pm \frac{3}{2} \right\rangle + c_5 \left| 0, \pm \frac{1}{2} \right\rangle + c_6 \left| \pm 1, \mp \frac{1}{2} \right\rangle \quad \text{for } E_{\pm 3} = E_c^{(1)}, \quad (13.26)$$

$$|\psi_{\pm 4}\rangle = c_7 \left| \mp 1, \pm \frac{3}{2} \right\rangle + c_8 \left| 0, \pm \frac{1}{2} \right\rangle + c_9 \left| \pm 1, \mp \frac{1}{2} \right\rangle \quad \text{for } E_{\pm 4} = E_c^{(2)}. \quad (13.27)$$

where the parameters c_i ($i = 1 - 9$) are defined by

$$\begin{aligned} c_1 &= \frac{\sqrt{6}}{\zeta_0} \beta_0, & c_2 &= -\beta_0, & c_3 &= \frac{\sqrt{8}}{\zeta_0 + 2} \beta_0, \\ c_4 &= \frac{\sqrt{6}}{\zeta_1} \beta_1, & c_5 &= -\beta_1, & c_6 &= \frac{\sqrt{8}}{\zeta_0 + 2} \beta_1, \\ c_7 &= \frac{\sqrt{6}}{\zeta_2} \beta_2, & c_8 &= -\beta_2, & c_9 &= \frac{\sqrt{8}}{\zeta_0 + 2} \beta_2, \end{aligned} \quad (13.28)$$

with

$$\beta_j = \left[\frac{6}{\zeta_j} + 1 + \frac{8}{(\zeta_j + 2)^2} \right]^{-1/2} \quad (j = 0, 1, 2).$$

The parameter ζ_j ($j = 0, 1, 2$) is related to $E_c^{(j)}/\lambda'$ as

$$\frac{E_c(j)}{\lambda'} = -\frac{x}{3} + \frac{3}{4}(\zeta_j + 3), \quad (13.29)$$

and

$$x = \frac{\delta}{\lambda'} = \frac{3}{4}(\zeta_j + 3) - \frac{9}{2\zeta_j} - \frac{6}{\zeta_j + 2}. \quad (13.30)$$

The wave functions $|\psi_{\pm 2}\rangle$ and $|\psi_{\pm 5}\rangle$ for $m = \pm 3/2$ are given by

$$|\psi_{\pm 2}\rangle = d_1 \left| 0, \pm \frac{3}{2} \right\rangle + d_2 \left| \pm 1, \pm \frac{1}{2} \right\rangle \quad \text{for } E_{\pm 2} = E_q^{(+)}, \quad (13.31)$$

$$|\psi_{\pm 5}\rangle = d_3 \left| 0, \pm \frac{3}{2} \right\rangle + d_4 \left| \pm 1, \pm \frac{1}{2} \right\rangle \quad \text{for } E_{\pm 5} = E_q^{(-)}, \quad (13.32)$$

where the parameter d_i ($i = 1-4$) is defined by

$$d_1 = \frac{9}{2\sqrt{6}}\gamma^{(+)}, \quad d_2 = \gamma^{(+)}\left(\frac{2}{3}x + \frac{E_q^{(+)}}{\lambda'}\right), \quad (13.33)$$

$$d_3 = \frac{9}{2\sqrt{6}}\gamma^{(-)}, \quad d_4 = \gamma^{(+)}\left(\frac{2}{3}x + \frac{E_q^{(+)}}{\lambda'}\right), \quad (13.34)$$

with

$$\gamma^{(\pm)} = \left[\left(\frac{9}{2\sqrt{6}} \right)^2 + \left(\frac{2}{3}x + \frac{E_q^{(\pm)}}{\lambda'} \right)^2 \right]^{-1/2}. \quad (13.35)$$

B. Fictitious spin $s = 1/2$

Since there are only two states in this lowest Kramers doublet ($E = E_c^{(0)}$), the true spin \mathbf{S} ($= 3/2$) can be replaced by a fictitious spin \mathbf{s} of the magnitude $1/2$ within the ground state. The g -factors can be evaluated as $g_c = g_c^{(0)} + \Delta g$ and $g_a = g_a^{(0)} + \Delta g$, where Δg is due to the effect of spin-orbit coupling in admixing the upper orbital levels into the ground orbital triplet. The values of $g_c^{(0)}$ and $g_a^{(0)}$, are given by

$$g_c^{(0)} = 2\langle \psi_{\pm 1} | V_z | \psi_{\pm 1} \rangle = (3k+6)c_1^2 + 2c_2^2 - (3k+2)c_3^2, \quad (13.36)$$

$$g_a^{(0)} = 2\langle \psi_{\pm 1} | V_x | \psi_{\mp 1} \rangle = 4\sqrt{3}c_1c_2 + 4c_2^2 - 3\sqrt{2}kc_2c_3 \quad (13.37)$$

with

$$V_z = -(3k/2)l_z + 2S_z, \quad V_x = -(3k/2)l_x + 2S_x.$$

If we take the z axis parallel to the c axis, and x, y axes perpendicular to it, we may finally replace the true spin $\mathbf{S} = 3/2$ within the ground doublet, by the $s = 1/2$ fictitious spin,

$$S_x = qs_x, S_y = qs_y, S_z = ps_z;$$

$$p = 2\langle \psi_{\pm 1} | \pm S_z | \psi_{\pm 1} \rangle = 3c_1^2 + c_2^2 - 3c_3^2, \quad (13.38)$$

$$q = 2\langle \psi_{\pm 1} | S_x \pm iS_y | \psi_{\mp 1} \rangle = 2\sqrt{3}c_1c_2 + 2c_2^2. \quad (13.39)$$

Let us now consider the Heisenberg exchange interaction given by

$$H = -2J_0 \mathbf{S}_i \cdot \mathbf{S}_j = -2J_0 q^2 \mathbf{s}_i \cdot \mathbf{s}_j - 2J_0 (p^2 - q^2) s_{iz} \cdot s_{jz}, \quad (13.40)$$

or

$$H = -2J \sum_{\langle i,j \rangle} \mathbf{s}_i \cdot \mathbf{s}_j - 2J_A \sum_{\langle i,j \rangle} s_{iz} s_{jz}. \quad (13.41)$$

where

$$J = q^2 J_0, \quad J_A = (p^2/q^2 - 1)J.$$

The first term is a Heisenberg-type (isotropic) exchange interaction and the second term is an anisotropic exchange interaction: $J_A = J_0 (p^2 - q^2)$. Since $s = 1/2$, there is no single ion anisotropy. The ratio $J_A/J (= p^2/q^2 - 1)$ provides a measure for the spin symmetry of the system. The spin dimensionality of the system is Ising-like for $J_A > 0$, XY-like for $J_A < 0$, and Heisenberg-like for $J_A = 0$.

C. Mathematica program: energy diagram of Co^{2+} in the trigonal field

Here we calculate the energy levels, the probability amplitudes and parameters of spin Hamiltonian of Co^{2+} ion in the trigonal field.

((Mathematica program))

Six Kramers doublets in Co^{2+} , M.E. Lines, Phys. Rev. 131, 546 (1963);

T. Oguchi, J. Phys. Soc. Jpn.

20, 2236 (1965))

Energy levels, E_t , $E_{c0} = E_c^{(0)}$, $E_{c1} = E_c^{(1)}$, $E_{c2} = E_c^{(2)}$, $E_{qn} = E_q^{(-)}$, $E_{qp} = E_q^{(+)}$

Clear["Global`"]

$$E_t = \frac{x}{3} + \frac{9}{4}; \quad E_{qp} = -\frac{x}{6} + \frac{3}{8} - \frac{1}{2} \sqrt{x^2 + \frac{3}{2}x + \frac{225}{16}};$$

$$E_{qn} = -\frac{x}{6} + \frac{3}{8} + \frac{1}{2} \sqrt{x^2 + \frac{3}{2}x + \frac{225}{16}};$$

$$E_{c0}[x3_] := \text{Module}[\{t, y\}, t = x3; \text{eq1} = t == \frac{3}{4}(y+3) - \frac{9}{2y} - \frac{6}{y+2};$$

$$s1 = \text{NSolve}[\text{eq1}, y] // \text{Flatten}; \quad E_{c0}[t] = -\left(-\frac{t}{3} + \frac{3}{4}(y+3)\right) /. s1[[3]]];$$

$$E_{c1}[x2_] := \text{Module}[\{t, y\}, t = x2; \text{eq1} = t == \frac{3}{4}(y+3) - \frac{9}{2y} - \frac{6}{y+2};$$

$$s1 = \text{NSolve}[\text{eq1}, y] // \text{Flatten}; \quad E_{c1}[t] = -\left(-\frac{t}{3} + \frac{3}{4}(y+3)\right) /. s1[[1]]];$$

$$E_{c2}[x1_] := \text{Module}[\{t, y\}, t = x1; \text{eq1} = t == \frac{3}{4}(y+3) - \frac{9}{2y} - \frac{6}{y+2};$$

$$s1 = \text{NSolve}[\text{eq1}, y] // \text{Flatten}; \quad E_{c2}[t] = -\left(-\frac{t}{3} + \frac{3}{4}(y+3)\right) /. s1[[2]]]$$

Since there are only two states in the lowest Kramers doublet, we can use a fictitious spin s for the lowest doublet.

Parameters, c1, c2, c3, c4, c5, c6, c7, c8, c9, d1, d2, d3, d4, p, q, gc, ga

```

c1[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

  c1[t, k] =  $\frac{\frac{\sqrt{6}}{y}}{\sqrt{\frac{6}{y^2} + 1 + \frac{8}{(y+2)^2}}}$  /. s4[[3]];

c2[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

  c2[t, k] =  $\frac{-1}{\sqrt{\frac{6}{y^2} + 1 + \frac{8}{(y+2)^2}}}$  /. s4[[3]];

c3[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

  c3[t, k] =  $\frac{\frac{\sqrt{8}}{y+2}}{\sqrt{\frac{6}{y^2} + 1 + \frac{8}{(y+2)^2}}}$  /. s4[[3]];

c4[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

  c4[t, k] =  $\frac{\frac{\sqrt{6}}{y}}{\sqrt{\frac{6}{y^2} + 1 + \frac{8}{(y+2)^2}}}$  /. s4[[1]];

c5[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

  c5[t, k] =  $\frac{-1}{\sqrt{\frac{6}{y^2} + 1 + \frac{8}{(y+2)^2}}}$  /. s4[[1]];

c6[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

  c6[t, k] =  $\frac{\frac{\sqrt{8}}{y+2}}{\sqrt{\frac{6}{y^2} + 1 + \frac{8}{(y+2)^2}}}$  /. s4[[1]];

c7[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

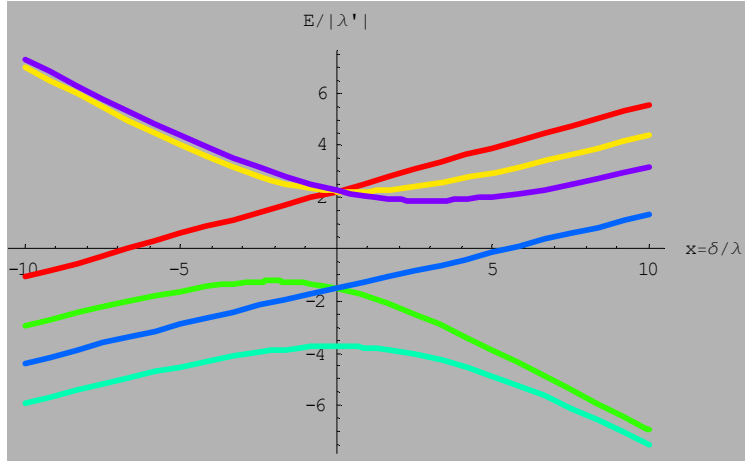
  c7[t, k] =  $\frac{\frac{\sqrt{6}}{y}}{\sqrt{\frac{6}{y^2} + 1 + \frac{8}{(y+2)^2}}}$  /. s4[[2]];

c8[x4_, k1_] := Module[{t, y, k}, t = x4; k = k1;
  eq44 = t ==  $\frac{3}{4} (y + 3) - \frac{9}{2y} - \frac{6}{y+2}$ ; s4 = NSolve[eq44, y] // Flatten;

```

Energy diagram of $E_t, E_{q^-}, E_{q^+}, E_c^0, E_c^1, E_c^2$ for Co^{2+} as a function of x

```
Plot[Evaluate[{Et, Eqn, Eqp, Ec0[x], Ec1[x], Ec2[x]}], {x, -10, 10}, PlotStyle->Table[Hue[0.15 i], {i, 0, 6}], Prolog->AbsoluteThickness[3], Background->GrayLevel[0.7], AxesLabel->{"x= $\delta/\lambda'$ ", "E/ $|\lambda'|$ "}]
```

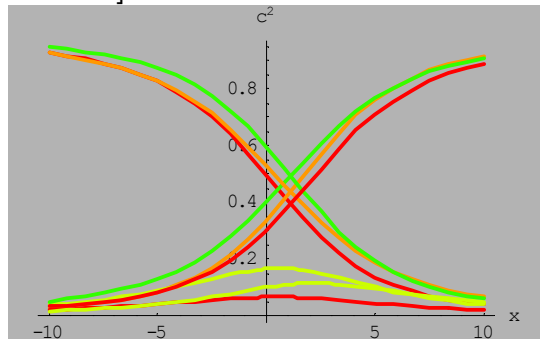


-Graphics-

Fig.47 Energy levels of six Kramers doublets for Co^{2+} ion in the trigonal field. E_c^0 (light green), E_{q^-} (green), E_c^1 (blue), E_c^2 (purple), E_{q^+} (yellow), and E_s (red)

Squares of parameters, $c_1, c_2, c_3, c_4, c_5, c_6$ as a function of x
 $k = 0.9$

```
Plot[Evaluate[{c1[x, 0.9]^2, c2[x, 0.9]^2, c3[x, 0.9]^2, c4[x, 0.9]^2, c5[x, 0.9]^2, c6[x, 0.9]^2, c7[x, 0.9]^2, c8[x, 0.9]^2, c9[x, 0.9]^2}], {x, -10, 10}, PlotStyle->Table[Hue[0.1 i], {i, 0, 3}], Background->GrayLevel[0.7], AxesLabel->{"x", "c^2"}, Prolog->AbsoluteThickness[2]]
```

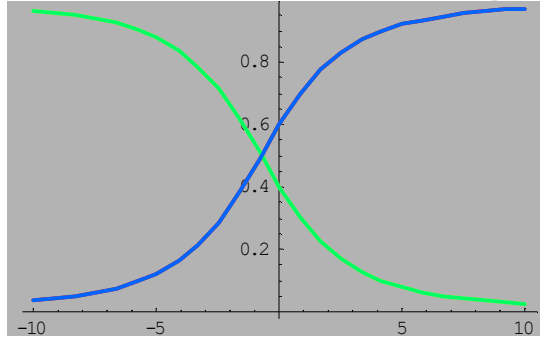


-Graphics-

Fig.48 Plot of the probability amplitudes c_n^2 ($n = 1 - 9$) for Co^{2+} ion in the trigonal field. $k = 0.9$.

Squares of parameters, $c_1, c_2, c_3, c_4, c_5, c_6$ as a function of x
 $k = 0.9$


```
Plot[Evaluate[{d1[x, 0.9]^2, d2[x, 0.9]^2, d3[x, 0.9]^2, d4[x, 0.9]^2}],
{x, -10, 10}, PlotStyle->Table[Hue[0.2 i], {i, 0, 3}],
Prolog->AbsoluteThickness[2], Background->GrayLevel[0.7]]
```

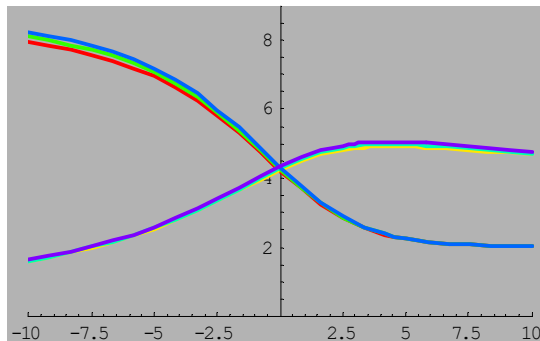


-Graphics-

Fig.49 Plot of the probability amplitudes d_n^2 ($n = 1 - 4$) for Co^{2+} ion in the trigonal field. $k = 0.9$.

*gc and ga, Lande g-factors along the c and a axes as a function of x
k = 0.0, 0.95, 1.0*

```
plc=Plot[Evaluate[Table[{gc[x,k], ga[x,k]}, {k, 0.9, 1.0, 0.05}]]
, {x, -10, 10}, Prolog->AbsoluteThickness[2], PlotStyle->Table[Hue[0.15
i], {i, 0, 5}], PlotRange->{{-10, 10}, {0, 9}},
Background->GrayLevel[0.7]]
```



-Graphics-

Fig.50 Plot of g_c and g_a as a function of x for Co^{2+} in the trigonal field. $k = 0.9, 0.95, \text{ and } 1$. $g_c > g_a$ for $x < 0$. $g_c < g_a$ for $x > 0$.

*Plot of gc vs ga
k = 0.9, 0.95, 1*

```
p1=ParametricPlot[Evaluate[Table[{gc[x,k], ga[x,k]}, {k, 0.9, 1.0, 0.05}]]], {x, -200, 100},
Prolog->AbsoluteThickness[2], AxesLabel->{"gc", "ga"},
PlotStyle->Table[Hue[0.3
```

```
i], {i, 0, 5}], PlotRange -> {{0, 10}, {0, 6}},
Background -> GrayLevel[0.7]]
```

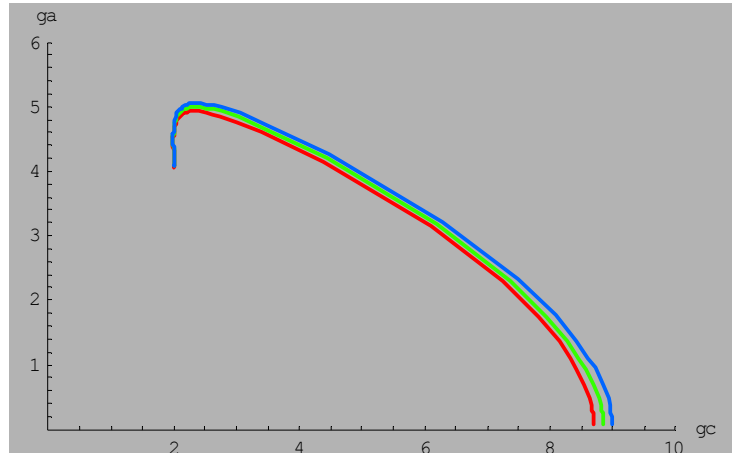
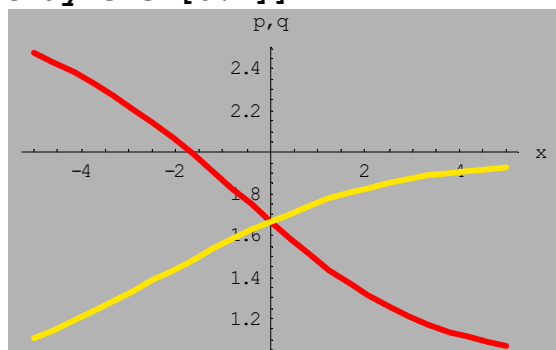


Fig.51 Calculated g_c and g_a -values of Co^{2+} ion in the trigonal field. $k = 0.9$ (red), 0.95 (green), and 1.0 (blue).

Parameters p and q as a function of x
 $k = 0.8, 0.9, 1.0, 1.1$

```
Plot[Evaluate[Table[{p[x, k], q[x, k]}, {k, 0.8, 1.1, 0.1}]], {x, -5, 5},
PlotStyle -> Table[Hue[0.15 i], {i, 0, 6}], Prolog -> AbsoluteThickness[3],
AxesLabel -> {"x", "p, q"}, Background -> GrayLevel[0.7]]
```



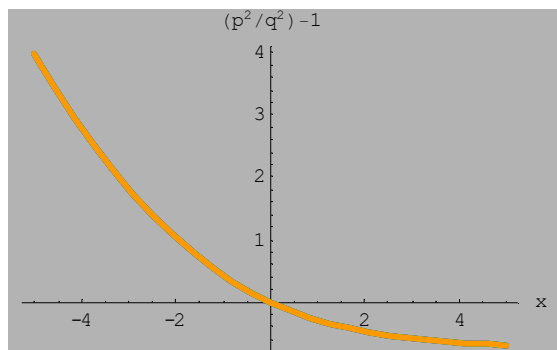
-Graphics-

Fig.52 Plot of the parameters p (red) and q (yellow) as a function of x for Co^{2+} ion in the trigonal field. $k = 0.8, 0.9, 1.0,$ and 1.0 .

Parameter $\frac{p^2}{q^2} - 1$ as a function of x

$k = 0.8, 0.9, 1.0, 1.1$

```
Plot[Evaluate[Table[p[x, k]^2/q[x, k]^2 - 1, {k, 0.8, 1.1, 0.1}]],
{x, -5, 5}, PlotStyle -> Table[Hue[0.7 i], {i, 0, 6}],
Prolog -> AbsoluteThickness[3], AxesLabel -> {"x", "(p^2/q^2)-1"},
Background -> GrayLevel[0.7]]
```



-Graphics-

Fig.53 Plot of $p^2/q^2 - 1$ as a function of x for Co^{2+} ion in the trigonal field. $k = 0.8, 0.9, 1.0$, and 1.0 .

14. CONCLUSION

We have shown that the spin Hamiltonian well accurately describes the magnetic properties of magnetic ions in the crystal field. When these magnetic ions are magnetically coupled through exchange interactions, they may undergo a second-order phase transition at a critical temperature [Curie temperature (ferromagnet) or a Néel temperature (antiferromagnet)]. Spins are ordered below the critical temperature. The static critical exponents depend on the dimensionality ($d = 3, 2$) of the system and the symmetry dimensionality of the order parameter [Ising ($n = 1$), XY ($n = 2$), and Heisenberg ($n = 3$)]. The spin dimensionality can be determined from the spin Hamiltonian.²¹ In two dimensions, there are phase transitions for the Ising and XY spin symmetry. For example, K_2CoF_4 and Rb_2CoF_4 are two-dimensional (2D) Ising-like antiferromagnet (fictitious spin 1/2), and K_2MnF_4 is a 2D Heisenberg antiferromagnet. In contrast, K_2CuF_4 (spin 1/2) is a 2D XY -like ferromagnet.²² For the 2D Ising model, there is an exact Onsager solution,²³ while for the 2D XY model, the system is predicted to show a Kosterlitz-Thouless (KT) transition.²⁴ The spins form vortices at low temperatures, and below the KT transition temperature the vortices become bound. The critical exponents of critical behaviors of the spin systems with short range interactions depends only on the dimensionality d and the spin dimensionality n (the universality).

Since the beginning of 1980's, we have been studying the magnetic phase transitions of quasi 2D spin systems such as stage-2 CoCl_2 -, NiCl_2 -, CuCl_2 -, FeCl_3 -, MnCl_2 -, and CrCl_3 - graphite intercalation compounds.²⁵⁻³¹ We find that the magnetic properties of these compounds are well described by the appropriate spin Hamiltonians of Co^{2+} , Ni^{2+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , and Cr^{3+} in the trigonal crystal field.

REFERENCES

1. C. Kittel, Introduction to Solid State Physics, seventh edition (John Wiley & Sons, Inc., New York, 1996).
2. J.H. Van Vleck, Nobel Lecture (December 8, 1977), *Quantum Mechanics The Key to Understanding Magnetism*.
3. R.M. White, *Quantum Theory of Magnetism* (Springer-Verlag, New York, 2007).
4. K. Yosida, *Theory of Magnetism* (Springer-Verlag, Berlin, 1996).
5. J. Kanamori, *Magnetism* (Baifukan, Tokyo, 1969, in Japanese).

6. M. Date, *Electron Spin Resonance* (Baifukan, Tokyo, 1978, in Japanese).
7. L. Hoddeson, E. Braun, J. Teichmann, and S. Weart, *Out of the Crystal Maze* (Oxford University Press, New York, 1992).
8. J.H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932).
9. E.C. Stoner, *Magnetism and Matter* (Methuen, London, 1934).
10. J.S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, Cambridge, 1961).
11. A. Abraham and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).
12. S. Sugano, T. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic Press, New York, 1993).
13. T. Inui, Y. Tanabe, and Y. Onodera, *Group Theory and Its Applications in Physics* (Springer-Verlag, Berlin, 1990).
14. C.J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962).
15. K.W.H. Stevens, in *Magnetism* Vol.1 p1-22, edited by G.T. Rado and H. Suhl (Academic Press, New York 1963).
16. A. Abraham and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A205**, 135 (1951).
17. B. Bleaney and K.W.H. Stevens, *Reports on Progress in Physics* **16**, 108 (1953).
18. K. Inomata and T. Oguchi, *J. Phys. Soc. Jpn.* **23**, 765 (1967).
19. M.E. Lines, *Phys. Rev.* **131**, 546 (1963).
20. T. Oguchi, *J. Phys. Soc. Jpn.* **20**, 2236 (1965).
21. M.F. Collins, *Magnetic Critical Scattering* (Oxford University Press, New York, 1989).
22. L.J. de Jongh and A.R. Miedema, *Advances in Physics* **50**, 947 (2001).
23. L. Onsager, *Phys. Rev.* **65**, 117 (1944).
24. J.M. Kosterlitz and D.J. Thouless, *J. Phys. C* **6**, 1181 (1973).
25. T. Enoki, M. Suzuki, and M. Endo, *Graphite Intercalation Compounds and Applications* (Oxford University Press, Oxford, 2003). Chapter 7. (review).
26. M. Suzuki and I.S. Suzuki, *Phys. Rev. B* **57**, 10674 (1998). (stage-2 CrCl₃ GIC).
27. D.G. Wiesler, M. Suzuki, I.S. Suzuki, and N. Rosov, *Phys. Rev. B.* **55**, 6382 (1997). (stage-2 MnCl₂ GIC).
28. M. Suzuki and I.S. Suzuki, *Phys. Rev. B* **58**, 371 (1998). (stage-2 FeCl₃ GIC).
29. M. Suzuki and I.S. Suzuki, *Phys. Rev. B* **58**, 840 (1998). (stage-2 CoCl₂ GIC).
30. I.S. Suzuki and M. Suzuki, *J. Phys. Cond. Matter* **10**, 5399 (1998). (stage-2 NiCl₂ GIC).
31. M. Suzuki, I.S. Suzuki, C.R. Burr, D.G. Wiesler, N. Rosov, and K. Koga, *Phys. Rev. B* **50**, 9188 (1994). (stage-2 CuCl₂ GIC).

Appendix

A.1 perturbation theory for the non-degenerate case

The Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1, \quad (\text{A.1})$$

where \hat{H}_0 is an unperturbed Hamiltonian and \hat{H}_1 is the perturbation. $|\psi_n^{(0)}\rangle$ is the eigenket of \hat{H}_0 with an eigenvalue $E_n^{(0)}$ (non-degenerate case).

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle. \quad (\text{A.2})$$

Then the perturbation energy and the new eigenket are given by

$$E_n = E_n^{(0)} + \lambda \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle + \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} + \dots \quad (\text{A.3})$$

$$\begin{aligned} |\psi_n\rangle &= |\psi_n^{(0)}\rangle + \lambda \sum_{k \neq n} |\psi_k^{(0)}\rangle \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} \\ &+ \sum_{l \neq n} \sum_{k \neq n} |\psi_k^{(0)}\rangle \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} + \dots \end{aligned} \quad (\text{A.4})$$

A.2 Kramers theorem for N particles with spin 1/2

For spin 1/2, the time reversal operator is defined by

$$\hat{\Theta} = \eta \exp\left(-\frac{i}{\hbar} \hat{S}_y \pi\right) \hat{K} = -i \eta \hat{\sigma}_y \hat{K}, \quad (\text{A.5})$$

where \hat{K} is an operator which takes the complex conjugate and $-i \hat{\sigma}_y$ is a unitary operator.

Suppose that $|\psi\rangle$ is described by

$$|\psi\rangle = C_+|+\rangle + C_-|-\rangle, \quad (\text{A.6})$$

where C_+ and C_- are complex numbers. Then the time reversal state is given by

$$\begin{aligned} |\tilde{\psi}\rangle &= \hat{\Theta}|\psi\rangle = -i \eta \hat{\sigma}_y \hat{K} (C_+|+\rangle + C_-|-\rangle) = -i \eta \hat{\sigma}_y (C_+^*|+\rangle + C_-^*|-\rangle) \\ &= -i \eta (C_+^* \hat{\sigma}_y |+\rangle + C_-^* \hat{\sigma}_y |-\rangle) = \eta (C_+^* |-\rangle - C_-^* |+\rangle) \end{aligned}$$

since $\hat{\sigma}_y |+\rangle = i |-\rangle$, and $\hat{\sigma}_y |-\rangle = -i |+\rangle$. We again apply $\hat{\Theta}$ to $|\tilde{\psi}\rangle$

$$\begin{aligned} \hat{\Theta}^2 |\psi\rangle &= \hat{\Theta} [\eta (C_+^* |-\rangle - C_-^* |+\rangle)] = -i \eta \hat{\sigma}_y \hat{K} [\eta (C_+^* |-\rangle - C_-^* |+\rangle)] \\ &= -i \eta \hat{\sigma}_y [\eta^* (C_+ |-\rangle - C_- |+\rangle)] = -i [(C_+ \hat{\sigma}_y |-\rangle - C_- \hat{\sigma}_y |+\rangle)] \\ &= -i [(C_+ (-i) |+\rangle - C_- i |+\rangle)] = -(C_+ |+\rangle + C_- |-\rangle) = -|\psi\rangle \end{aligned}$$

or

$$\hat{\Theta}^2 = -\hat{1} \quad (\text{A.7})$$

We can show that

(i)

$$\hat{\Theta} \hat{\sigma}_x \hat{\Theta}^{-1} = -\hat{\sigma}_x, \quad (\text{A.8})$$

$$\hat{\Theta} \hat{\sigma}_y \hat{\Theta}^{-1} = -\hat{\sigma}_y, \quad (\text{A.9})$$

$$\hat{\Theta} \hat{\sigma}_z \hat{\Theta}^{-1} = -\hat{\sigma}_z. \quad (\text{A.10})$$

(ii) $|\psi\rangle$ and $|\tilde{\psi}\rangle = \hat{\Theta}|\psi\rangle$ are orthogonal, since $\langle \tilde{\psi} | \psi \rangle = \begin{pmatrix} -\eta^* C_- & \eta^* C_+ \\ C_+ & C_- \end{pmatrix} = 0$

We now consider the system with N electrons. N is an even or an odd integer number. For convenience we use $\eta = 1$. In general, the N -spins state $|\Phi\rangle$ is described by

$$\begin{aligned} |\Phi\rangle = & u_1 |+\rangle_1 |+\rangle_2 |+\rangle_3 |+\rangle_4 \dots |+\rangle_{N-1} |+\rangle_N + u_2 |+\rangle_1 |+\rangle_2 |+\rangle_3 |+\rangle_4 \dots |+\rangle_{N-1} |-\rangle_N \\ & + u_3 |+\rangle_1 |+\rangle_2 |+\rangle_3 |+\rangle_4 \dots |-\rangle_{N-1} |-\rangle_N + \dots + u_{2^N} |-\rangle_1 |-\rangle_2 |-\rangle_3 |-\rangle_4 \dots |-\rangle_{N-1} |-\rangle_N. \end{aligned} \quad (\text{A.11})$$

Since $-i\hat{\sigma}_y \hat{K} |+\rangle = |-\rangle$, and $-i\hat{\sigma}_y \hat{K} |-\rangle = -|+\rangle$, we have

$$\langle \Phi | \tilde{\Phi} \rangle = u_1^* (-1)^N u_{2^N}^* + u_1^* u_{2^N}^*$$

When N is odd, $\langle \Phi | \tilde{\Phi} \rangle = 0$, which means that $|\Phi\rangle$ and the time reversal state $|\tilde{\Phi}\rangle$ are independent states.