2022.4.13 Lecture 2

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

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Review

Chapter1 Basic Notions of Magnetism

Classical pictures of magnetic moments in materials:

- Magnetic charges
- Circular currents

Experimental methods to measure magnetization

Paramagnetic and diamagnetic terms in classical magnetization

Breakdown of classical magnetism: cancellation of paramagnetic and diamagnetic terms (Bohr-van Lewuuen theorem)

Introduction of spin angular momentum by relativistic quantum mechanics

Agenda

1. Spin-orbit interaction
2. Magnetism in quantum theory

Chapter 2 Magnetism in localized systems

1. Spherical potential
2. Larmor precession
3. Magnetism of inert gas
4. LS multiplex ground state of open shell ions and Hund’s rule

Magnetic moment of electron spin

Dirac eq. with electromagnetic field $i\hbar\frac{\partial\psi}{\partial t} = \left[c\boldsymbol{\alpha}(\boldsymbol{p}+e\boldsymbol{A}) + \beta m - e\phi\right]\psi$

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right) - c\sum_{j=x,y,z}\alpha_j\left(-i\hbar\frac{\partial}{\partial r_j}+eA_j\right) - \beta mc^2\right]\psi = 0$$

Operation from left: $i\hbar\frac{\partial}{\partial t}+e\phi + c\sum_{j=x,y,z}\alpha_j\left(-i\hbar\frac{\partial}{\partial r_j}+eA_j\right) + \beta mc^2$

We obtain

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)^2 - c^2(\boldsymbol{p}+e\boldsymbol{A})^2 - m^2c^4 + ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E}) + i\hbar c^2 e(\alpha_x\alpha_y B_z + \alpha_y\alpha_z B_x + \alpha_z\alpha_x B_y)\right]\psi = 0$$

Because $\alpha_x\alpha_y = i\sigma_z^{(4)}, \quad \alpha_y\alpha_z = i\sigma_x^{(4)}, \quad \alpha_z\alpha_x = i\sigma_y^{(4)}$

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)^2 - c^2(\boldsymbol{p}+e\boldsymbol{A})^2 - m^2c^4 + ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E}) - \hbar c^2 e\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\psi = 0$$

Magnetic moment of electron spin (2)

Stationary solution: $\psi(\boldsymbol{r},t)=\exp(-i\epsilon t/\hbar)\varphi(\boldsymbol{r})$

$$\left[(\epsilon+e\phi)^2-c^2(\boldsymbol{p}+e\boldsymbol{A})^2-m^2c^4+ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E})-\hbar c^2 e\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\varphi=0$$

$$\phi=0,\ \ \boldsymbol{E}=0$$

Low energy expansion

$$\epsilon=mc^2+\delta$$

We take first order in $\dfrac{\delta}{mc^2}$

$$\left[\frac{1}{2m}(\boldsymbol{p}+e\boldsymbol{A})^2+\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\varphi=\delta\varphi$$

Bohr magneton $\mu_{\mathrm{B}}\equiv\dfrac{e\hbar}{2m}\approx 9.274\times10^{-24}\ \mathrm{JT}^{-1}$

$$\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}=\mu_{\mathrm{B}}\boldsymbol{\sigma}\cdot\boldsymbol{B}=2\mu_{\mathrm{B}}\boldsymbol{s}\cdot\boldsymbol{B}$$

Therefore the magnetic moment is $-2\mu_{\mathrm{B}}\boldsymbol{s}$

Two-component separation approximation

Stationary Dirac equation $[c\boldsymbol{\alpha}\boldsymbol{p} + mc^2\beta]\varphi = \epsilon\varphi$

Pauli representation $\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$ 4 × 4 matrices

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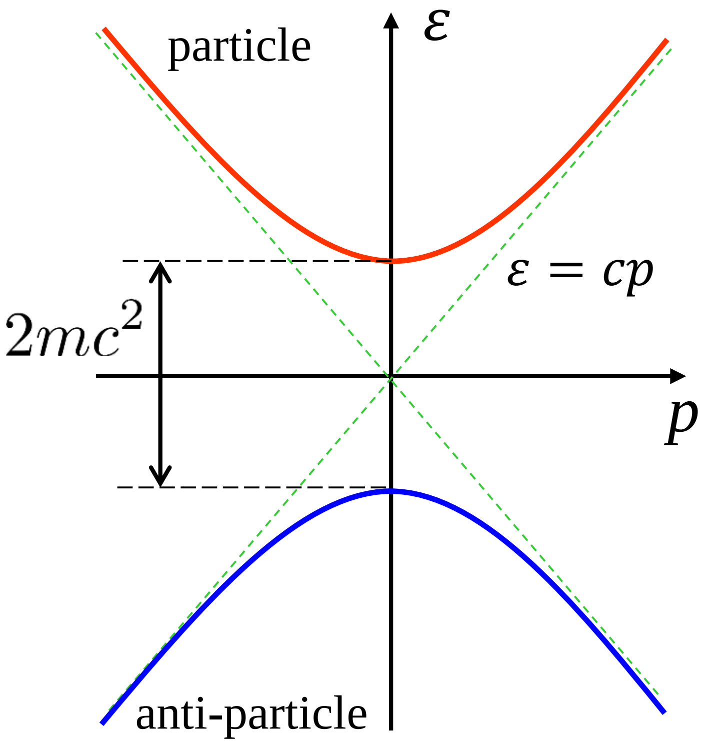
When the particle sits still: $\epsilon = \pm mc^2$



+ corresponds to *I*, – corresponds to –*I* in β

→ upper two laws: particle, lower two: anti-particle (?)

Finite momentum *p* requires correction.

$$\tan 2\theta = \frac{p}{mc} \qquad \psi_\uparrow = e^{i(kz-\omega t)} \begin{pmatrix} \cos\theta \\ 0 \\ \sin\theta \\ 0 \end{pmatrix}$$

Leak to lower laws

Spin-orbit interaction

Stationary equation $$(c\boldsymbol{\alpha}\cdot\boldsymbol{p}+\beta mc^2+V)\varphi=\epsilon\varphi$$

Two-component approximation $$\varphi=\begin{pmatrix}\varphi_{\mathrm{A}}\\ \varphi_{\mathrm{B}}\end{pmatrix}$$

Simultaneous equations $$\begin{cases}\boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi_{\mathrm{B}}=c^{-1}(\delta-V)\varphi_{\mathrm{A}},\\ \boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi_{\mathrm{A}}=c^{-1}(\delta-V+2mc^2)\varphi_{\mathrm{B}}.\end{cases}$$ $$\delta=\epsilon-mc^2$$

Erase of φ_{B} $$c^{-2}\boldsymbol{\sigma}\cdot\boldsymbol{p}(\delta-V+2mc^2)^{-1}\boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi_{\mathrm{A}}=(\delta-V)\varphi_{\mathrm{A}}$$

Low velocity ($p\ll mc$) expansion $$c^2(\delta-V+2mc^2)^{-1}\approx\frac{1}{2m}\left[1-\frac{\delta-V}{2mc^2}+\cdots\right]$$

Normalization condition $$\langle\varphi|\varphi\rangle=\langle\varphi_{\mathrm{A}}|\varphi_{\mathrm{A}}\rangle+\langle\varphi_{\mathrm{B}}|\varphi_{\mathrm{B}}\rangle=1$$

Spin-orbit interaction (2)

Introduction of magnetic field $\boldsymbol{p} \to \boldsymbol{p} + e\boldsymbol{A}$

Correction due to leakage $\langle \varphi_{\mathrm{B}} | \varphi_{\mathrm{B}} \rangle = \left\langle \varphi_{\mathrm{A}} \middle| \left[\frac{p^2 + e\hbar\boldsymbol{\sigma}\cdot\boldsymbol{B}}{4m^2c^2} \right] \middle| \varphi_{\mathrm{A}} \right\rangle = O\left(\frac{v^2}{c^2} \right)$

Corrected two-component wavefunction $\varphi_a = \left(1 + \frac{p^2 + e\hbar\boldsymbol{\sigma}\cdot\boldsymbol{B}}{8m^2c^2} \right) \varphi_{\mathrm{A}}$

Pauli two-component approximation

Zeeman Spin-orbit interaction

$$\left[\frac{p^2}{2m} + V + \boxed{\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}} - \boxed{\frac{e\hbar\boldsymbol{\sigma}\cdot\boldsymbol{p}\times\boldsymbol{E}}{4m^2c^2}} - \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\boldsymbol{E} - \frac{p^4}{8m^3c^2} - \frac{e\hbar p^2}{4m^3c^2}\boldsymbol{\sigma}\cdot\boldsymbol{B} - \frac{(e\hbar B)^2}{8m^3c^2} \right] \varphi_a = \delta\varphi_a$$

Quantum Mechanical Treatment of Magnetism

$$\mathcal{H} = \sum_n \left[\frac{1}{2m}(\boldsymbol{p}_n + e\boldsymbol{A}(\boldsymbol{r}_n))^2 + U(\boldsymbol{r}_n) + g\mu_{\mathrm{B}}\boldsymbol{s}_n \cdot \boldsymbol{B} \right] + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots)$$

Nucleus potential　　g-factor

Symmetric gauge　$\boldsymbol{A}(\boldsymbol{r}_n) = (\boldsymbol{B} \times \boldsymbol{r}_n)/2$

$$\mathcal{H} = \sum_n \left[\frac{\boldsymbol{p}_n^2}{2m} + U(\boldsymbol{r}_n) \right] + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots) \quad \cdots\cdots \quad \mathcal{H}_0$$

$\hbar \boldsymbol{l}_n \equiv \boldsymbol{r}_n \times \boldsymbol{p}_n$

$$+ \mu_{\mathrm{B}} \sum_n (\boldsymbol{l}_n + g\boldsymbol{s}_n) \cdot \boldsymbol{B} \quad \cdots\cdots \quad \mathcal{H}_1$$

$$+ \frac{e^2}{8m} \sum_n \{ r_n^2 B^2 - (\boldsymbol{B} \cdot \boldsymbol{r}_n)^2 \} \quad \cdots\cdots \quad \mathcal{H}_2$$

Magnetic moment

Commutation relations

$$\begin{cases} [r_{n\alpha}, p_{n\beta}] = r_{n\alpha}p_{n\beta} - p_{n\beta}r_{n\alpha} = i\hbar\delta_{\alpha\beta} \quad (\alpha, \beta = x, y, z) \\ [s_{n\alpha}, s_{n\beta}] = is_{n\gamma} \quad (\alpha, \beta, \gamma = x, y, z \text{ (cyclic)}) \\ [l_{n\alpha}, l_{n\beta}] = il_{n\gamma} \quad (\alpha, \beta, \gamma = x, y, z \text{ (cyclic)}) \end{cases}$$

Magnetic moment

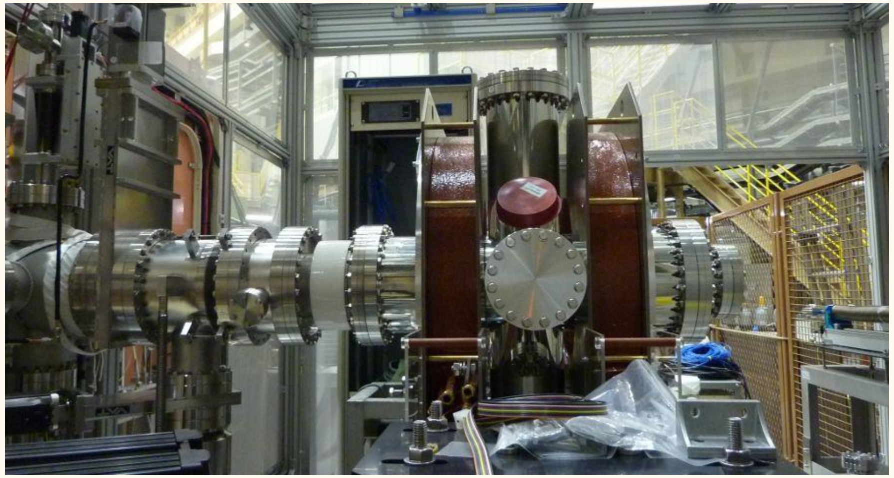
$$\begin{aligned} \mu = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{B}} &= -\mu_{\mathrm{B}} \sum_n (\boldsymbol{l}_n + g\boldsymbol{s}_n) - \frac{e^2}{4m} \sum_n \{r_n^2 \boldsymbol{B} - \boldsymbol{r}_n(\boldsymbol{r}_n \cdot \boldsymbol{B})\} \\ &= -\mu_{\mathrm{B}} \sum_n (\boldsymbol{l}_n + g\boldsymbol{s}_n) - \frac{e^2}{4m} \sum_n (\boldsymbol{r}_n \times (\boldsymbol{B} \times \boldsymbol{r}_n))\} \end{aligned}$$

Paramagnetic Diamagnetic

This expression does not have drastic changes other than spin magnetic moment.
However …

Comment: Spins of nucleons

Protons, Neutrons, Muons have spins.



MRI

J-PARC

KEK

NMR

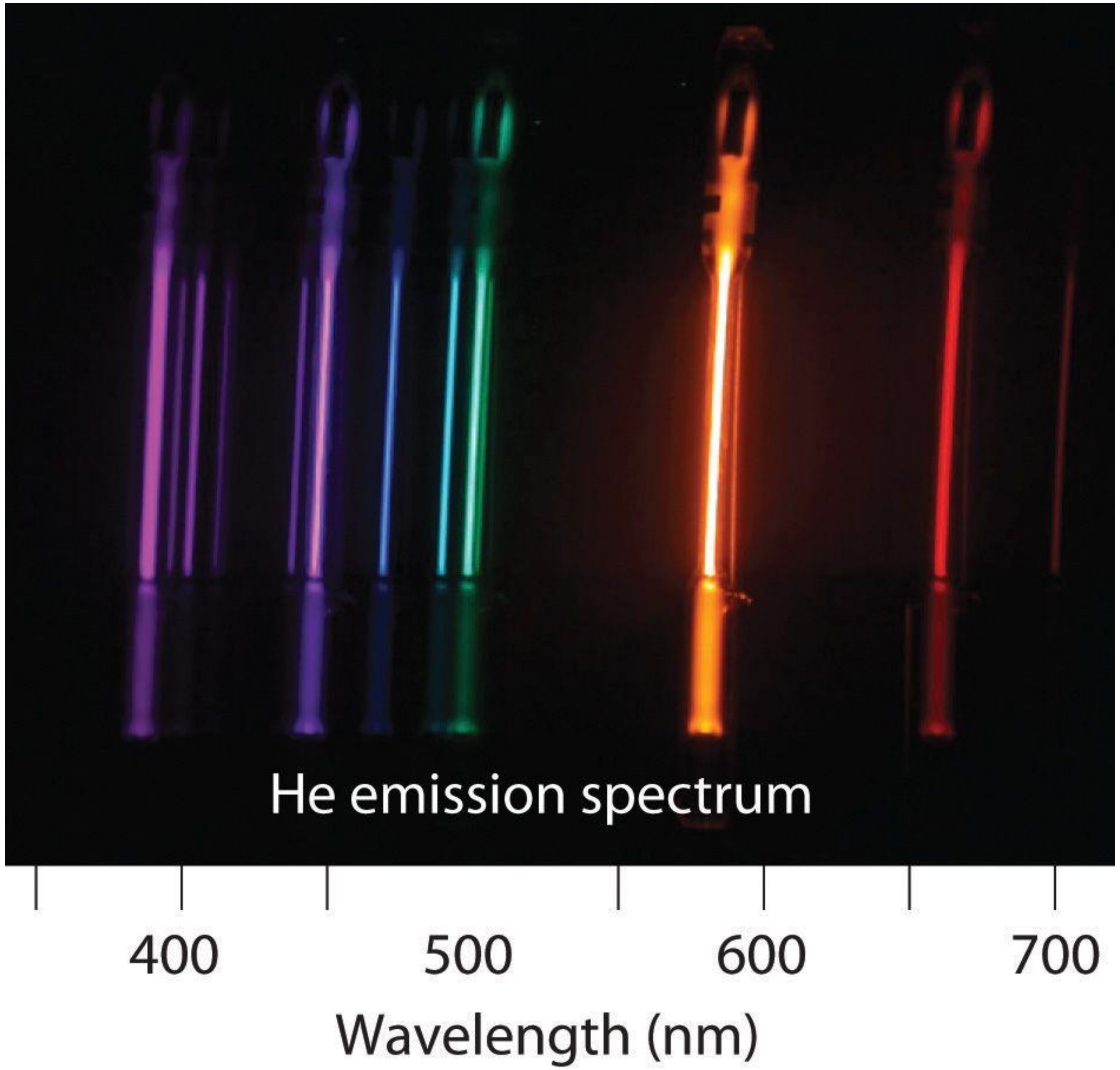
Neutron diffraction

μSR

Chapter 2

Magnetism of Localized Electrons

Star birth



Second quantization

$|\boldsymbol{n}\rangle = |n_1, n_2, \cdots\rangle$ Number representation
(index the state with number of particles occupying basis states)

$|0\rangle$ Vacuum

$a_j^\dagger |0\rangle = |1_j\rangle$ Creation operator of *j*-th state
(Hermitian conjugate: annihilation operator)

Fermion:
anti-commutation relation $[a_i, a_j]_+ = [a_i^\dagger, a_i^\dagger]_+ = 0, \quad [a_i, a_j^\dagger]_+ = \delta_{ij}$

number operator $\hat{n}_j \equiv a_j^\dagger a_j \qquad \hat{n}_j |\boldsymbol{n}\rangle = n_j |\boldsymbol{n}\rangle$

Boson: commutation relation $[b_i, b_j] = [b_i^\dagger, b_i^\dagger] = 0, \quad [b_i, b_j^\dagger] = \delta_{ij}$

$$|n_j\rangle = \frac{1}{\sqrt{n_j!}}(a_j^\dagger)^{n_j} |0\rangle$$

Operators in second quantization representation

Multiparticle operator $\mathcal{F}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots) = \sum_i f(\boldsymbol{r}_i)$

Slater determinant $|\psi_{1,2,\cdots}\rangle$

$$\langle\psi_{m_1,m_2,\cdots}|\,\mathcal{F}\,|\psi_{n_1,n_2,\cdots}\rangle = \sum_i \langle\psi_{m_1,m_2,\cdots}|\,f(\boldsymbol{r}_i)\,|\psi_{n_1,n_2,\cdots}\rangle$$

Second quantization

Particle statistics

Annihilation and creation operator (anti-)commutation relations

$$F = \sum_{mn} \langle m|f|n\rangle\, a_m^\dagger a_n$$

$$\langle m|f|n\rangle = \int d\boldsymbol{r}\phi_m^*(\boldsymbol{r})f(\boldsymbol{r})\psi_n(\boldsymbol{r})$$

$$\langle\psi_{m_1,m_2,\cdots}|\,\mathcal{F}\,|\psi_{n_1,n_2,\cdots}\rangle = \langle\boldsymbol{m}|F|\boldsymbol{n}\rangle$$

$$G = \frac{1}{2}\sum_{klmn} \langle kl|g|mn\rangle\, a_k^\dagger a_l^\dagger a_n a_m$$

Electrons in a central force potential

$$\mathcal{H}_{\rm L} = \mathcal{H}_{\rm L0} + \mathcal{H}_{\rm C} + \mathcal{H}_{\rm SOI} + \mathcal{H}_{\rm CF}$$

Localized system

crystal field

spin-orbit interaction

mutual Coulomb interaction

single-electron (non-interaction)

$$\mathcal{H}_{\rm L0} = \sum_j \left[\frac{\boldsymbol{p}_j^2}{2m} + V_{\rm sp}(r_j) \right]$$

Electrons in a central force (spherical) potential

Eigenfunction in polar coordinate: (r, θ, φ)

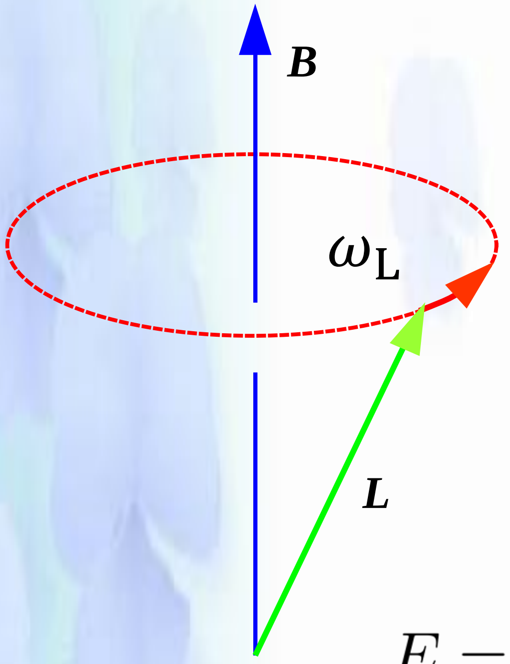
$$\psi_{nlm}(\boldsymbol{r}) = R_{nl}(r) Y_{lm}(\theta, \varphi)$$

Radial wavefunction $R_{nl}(r) = b_{nl}\rho^l e^{-\rho/2} L_{n+1}^{2l+1}(\rho), \quad \rho \equiv \frac{2}{n}\frac{r}{a_0}$

Eigen energy $\epsilon_{nl} = -\frac{R_\infty}{n^2}, \quad R_\infty = \frac{me^4}{8\epsilon_0 h^3 c}$

$$\mathcal{H}_{\rm L0} = \sum_{nl} \epsilon_{nl} \sum_{m\sigma} a^\dagger_{nlm\sigma} a_{nlm\sigma}$$

Larmor precession



Coulomb potential $$V_{\rm sp}(r_j) = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_j}$$

Total orbital angular momentum $$\hbar\boldsymbol{L} = \hbar\sum_i \boldsymbol{l}_i$$

$$\mathcal{H}_1 = \mu_{\rm B}\boldsymbol{L}\cdot\boldsymbol{B} = \mu_{\rm B}L_zB$$

Directional quantization $$L_z = M : -L,\ -L+1,\cdots,L-1,\ L$$

$$E = E_0 + \mu_{\rm B}MB \equiv E_0 + \hbar\omega_{\rm L}M, \quad \boxed{\omega_{\rm L} \equiv \frac{\mu_{\rm B}B}{\hbar} = \frac{eB}{2m}\ \text{(Larmor frequency)}}$$

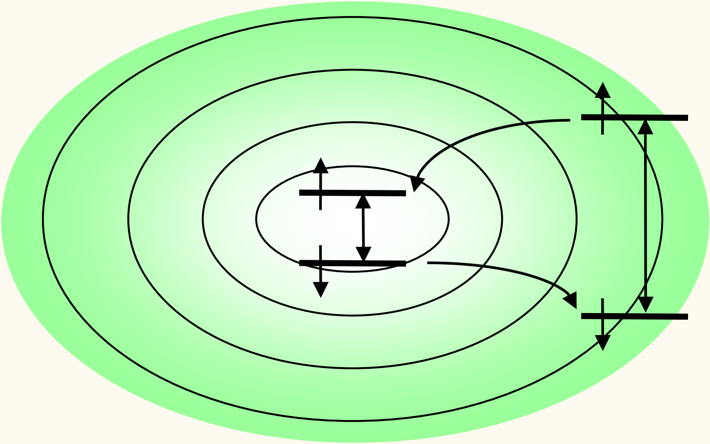
Heisenberg equation $$\frac{{\rm d}\boldsymbol{L}}{{\rm d}t} = \frac{1}{i\hbar}[\boldsymbol{L},\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2]$$

Larmor precession $$L_x(t) = L_0\cos(\omega_{\rm L}t+\theta_0), \quad L_y(t) = L_0\sin(\omega_{\rm L}t+\theta_0)$$

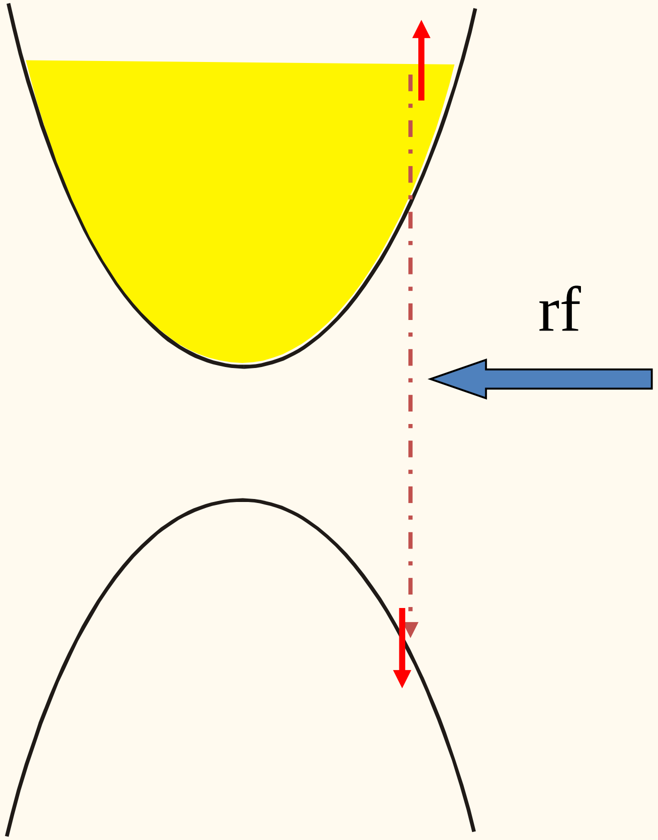
In the case of spin: g-factor $$\omega_{\rm L} = g\frac{eB}{2m} \approx \frac{eB}{m}$$

Magnetism of inert gases

Star birth



Magnetic trap



Evaporation cooling

Total angular momentum

$$\boldsymbol{L} = \sum_j \boldsymbol{l}_j = \sum_\sigma \sum_{mm'} \langle m|\, \boldsymbol{l}\, |m'\rangle_{nl}\, a^\dagger_{m\sigma} a_{m'\sigma},$$

$$\boldsymbol{S} = \sum_j \boldsymbol{s}_j = \sum_m \sum_{\sigma\sigma'} \left(\frac{\boldsymbol{\sigma}}{2}\right)_{\sigma\sigma'} a^\dagger_{m\sigma} a_{m\sigma'},$$

$$\boldsymbol{J} = \sum_j \boldsymbol{j}_j = \boldsymbol{L} + \boldsymbol{S}$$

Magnetism of inert gases

Inert gases: Closed shell structure $L = S = 0$ due to quantization!

Residual is the dielectric term: $\boldsymbol{\mu}_{\mathrm{dia}} = -\frac{e^2}{4m}\sum_n [\boldsymbol{r}_n \times (\boldsymbol{B} \times \boldsymbol{r}_n)]$

$$= -\frac{e}{2}\sum_n [\boldsymbol{r}_n \times (\boldsymbol{\omega}_{\mathrm{L}} \times \boldsymbol{r}_n)] = -\frac{\mu_{\mathrm{B}}}{\hbar}\sum_n [\boldsymbol{r}_n \times (m\boldsymbol{v}_n)]$$

Larmor rotation angular momentum

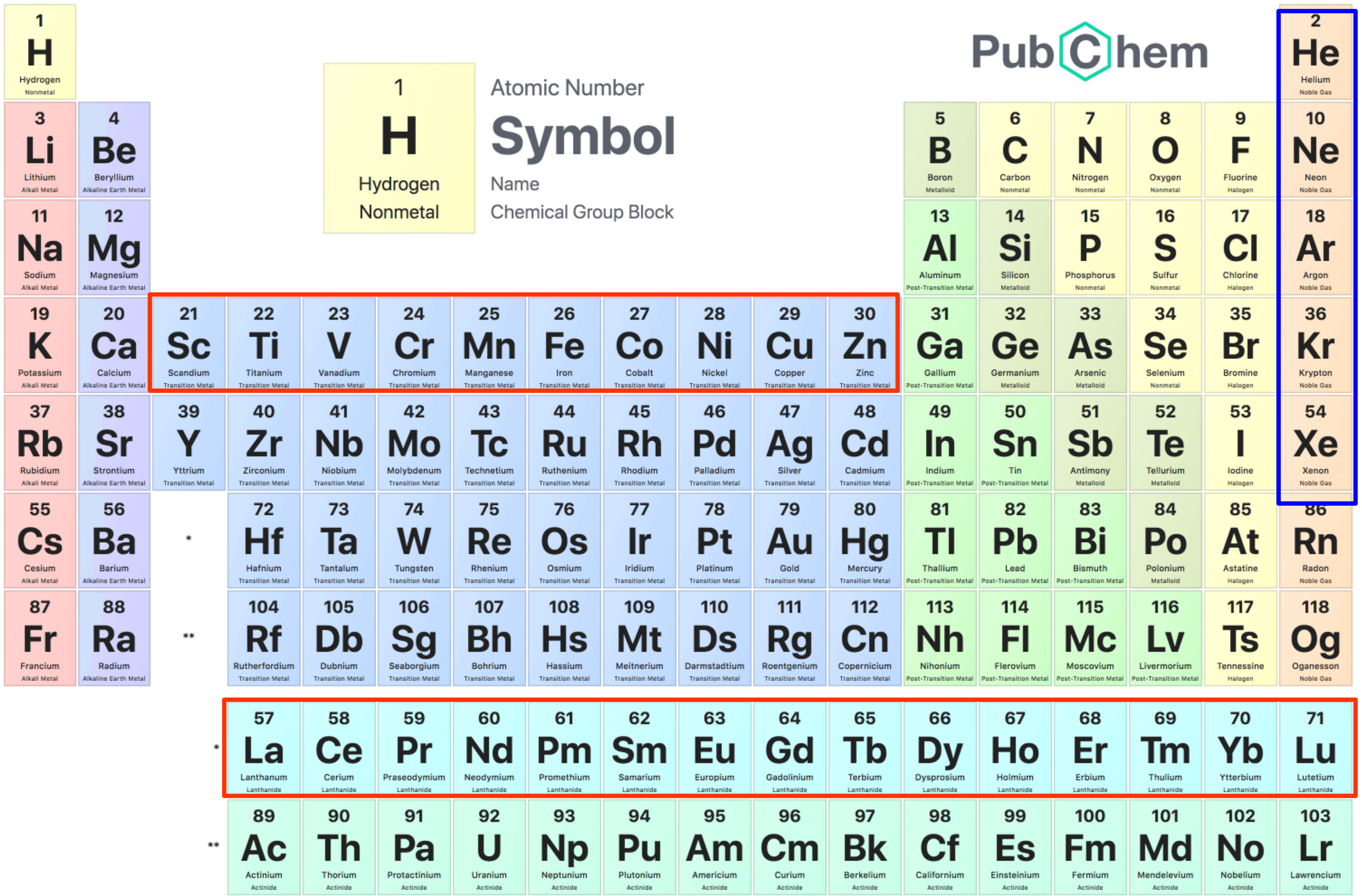
Z	Element	Susceptibility
2	He	-1.9×10^{-6}
10	Ne	-7.2×10^{-6}
18	Ar	-19.4×10^{-6}
36	Kr	-28×10^{-6}
54	Xe	-43×10^{-6}

$$\mu_{\mathrm{d}} = -\frac{e^2}{4m}\left\langle x^2 + y^2 \right\rangle B = -\frac{e^2}{6m}\left\langle r^2 \right\rangle B$$

$$\chi = -\frac{N_{\mathrm{A}} Z e^2 \left\langle r^2 \right\rangle}{6m}$$ Moll susceptibility

$$\frac{\left\langle r^2 \right\rangle}{a_{\mathrm{B}}^2} \sim ??$$

PERIODIC TABLE OF ELEMENTS



PubChem

1
H
Hydrogen
Nonmetal

Atomic Number
Symbol
Name
Chemical Group Block

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

Electronic states in magnetic ions

Open shell electronic states

Angular momentum *l* orbit $m = -l, -l+1, \cdots, l$

State of many electrons: indexed with *L* and *S* : state (*L*, *S*) degenerated in the absence of coulomb term

(*L*, *S*) term degenerated (2*L*+1)(2*S*+1) : LS multiplex

Which state is the ground state?

$$\mathcal{H}_\mathrm{C} = \frac{1}{2}\sum_{m_1,\cdots,m_4}\sum_{\sigma_1\sigma_2}\left\langle m_1 m_2 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_3 m_4 \right\rangle a^\dagger_{m_1\sigma_1} a^\dagger_{m_2\sigma_2} a_{m_3\sigma_3} a_{m_4\sigma_4}$$

$$\left\langle m_1 m_2 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_3 m_4 \right\rangle = \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 u^*_{m_1}(\boldsymbol{r}_1) u^*_{m_2}(\boldsymbol{r}_2) \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_1 - \boldsymbol{r}_2|} u_{m_3}(\boldsymbol{r}_2) u_{m_4}(\boldsymbol{r}_1)$$

Dominating terms

$$m_1 = m_2 = m_3 = m_4$$

$$\left\langle m_1 m_1 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_1 m_1 \right\rangle a^\dagger_{m_1\uparrow} a^\dagger_{m_1\downarrow} a_{m_1\uparrow} a_{m_1\downarrow} = U_0 \sum_m \hat{n}_{m\uparrow}\hat{n}_{m\downarrow} \quad (\hat{n}_{m\sigma} = a^\dagger_{m\sigma} a_{m\sigma})$$

Coulomb repulsion in the same orbit

$$m_1 = m_4 \neq m_2 = m_3$$

$$\frac{1}{2}\sum_{m_1 \neq m_2} U(m_1, m_2)\hat{n}_{m1}\hat{n}_{m2} \quad \left(\hat{n}_m = \sum_\sigma n_{m\sigma}\right)$$

Coulomb repulsion between different orbits

$$m_1 = m_3 \neq m_2 = m_4$$

Exchange term

$$\frac{1}{2}\sum_{m_1 \neq m_2}\sum_{\sigma_1\sigma_2} J(m_1, m_2) a^\dagger_{m_1\sigma_1} a^\dagger_{m_2\sigma_2} a_{m_1\sigma_2} a_{m_2\sigma_1}$$

$$= -\frac{1}{2}\sum_{m_1 \neq m_2} J(m_1, m_2)\left(\frac{1}{2}\hat{n}_{m_1}\hat{n}_{m_2} + 2\boldsymbol{s}_{m_1}\cdot\boldsymbol{s}_{m_2}\right)$$

Exchange integral

Spin operator $\boldsymbol{s}_m = \sum_{\sigma_1\sigma_2} \left(\frac{\boldsymbol{\sigma}}{2}\right)_{\sigma_1\sigma_2} a^{\dagger}_{m\sigma_1} a_{m\sigma_2}$

Exchange integral $J(m_1, m_2)$

$$
\begin{aligned}
J(m_1, m_2) &= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 u^*_{m_1}(\boldsymbol{r}_1) u_{m_2} \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_1 - \boldsymbol{r}_2|} u_{m_1}(\boldsymbol{r_2}) u^*_{m_2}(\boldsymbol{r_2}) \\
&= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 u^*_{m_1}(\boldsymbol{r}_1) u_{m_2} \left[\int d\boldsymbol{q} \frac{e^2}{\epsilon_0 q^2} e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_1 - \boldsymbol{r}_2)} \right] u_{m_1}(\boldsymbol{r_2}) u^*_{m_2}(\boldsymbol{r_2}) \\
&= \int d\boldsymbol{q} \frac{e^2}{\epsilon_0 q^2} \left| \int d\boldsymbol{r}_1 u^*_{m_1}(\boldsymbol{r}_1) u_{m_2}(\boldsymbol{r}_1) e^{i\boldsymbol{q}\cdot\boldsymbol{r}_1} \right|^2 > 0
\end{aligned}
$$

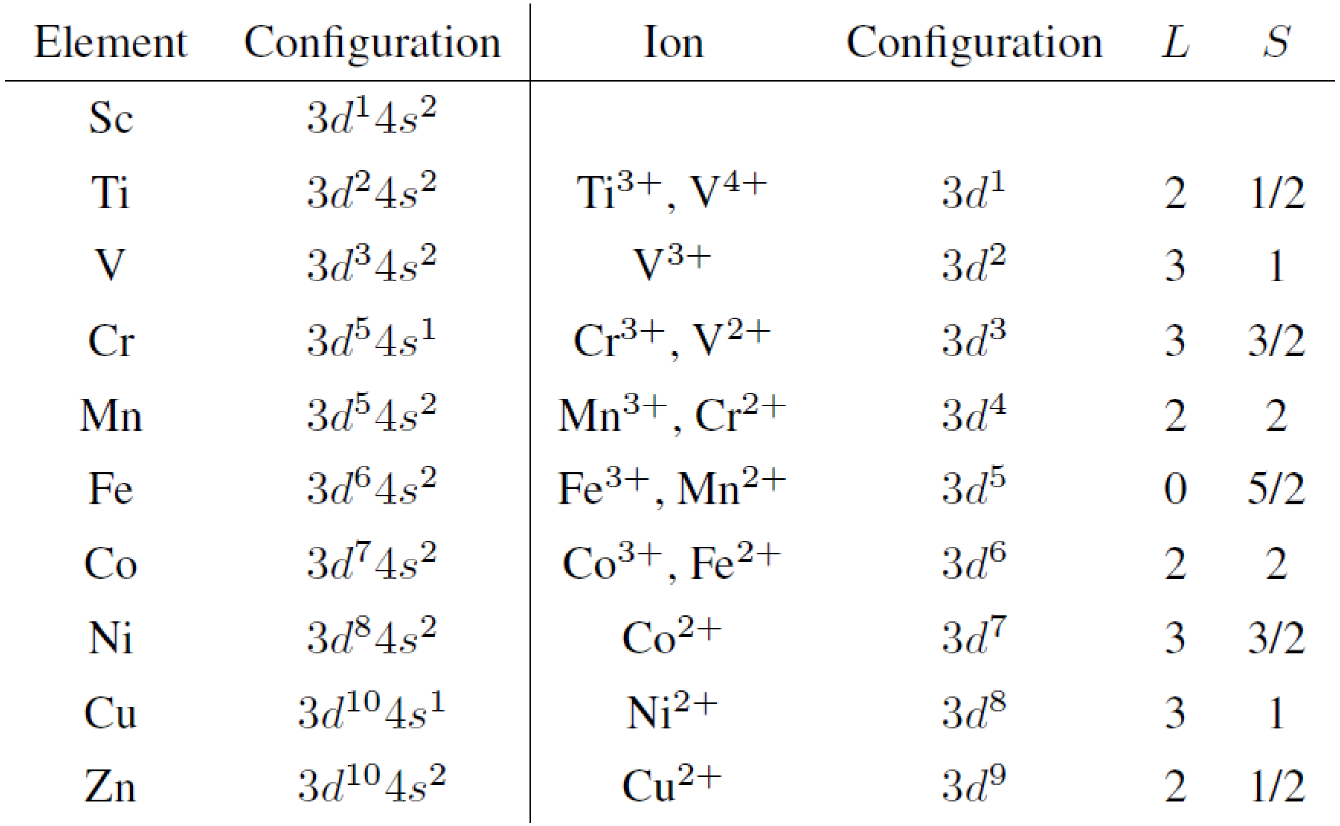
Hund’s rule

Hund’s rule

The ground LS multiplex is determined by the following

1. It should have maximum *S*.
2. Under the condition 1., it should have maximum *L*.

3d transition metal ions



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

Summary

1. Spin-orbit interaction
2. Magnetism in quantum theory

Chapter 2 Magnetism in localized systems

1. Spherical potential
2. Larmor precession
3. Magnetism of inert gas
4. LS multiplex ground state of open shell ions and Hund’s rule