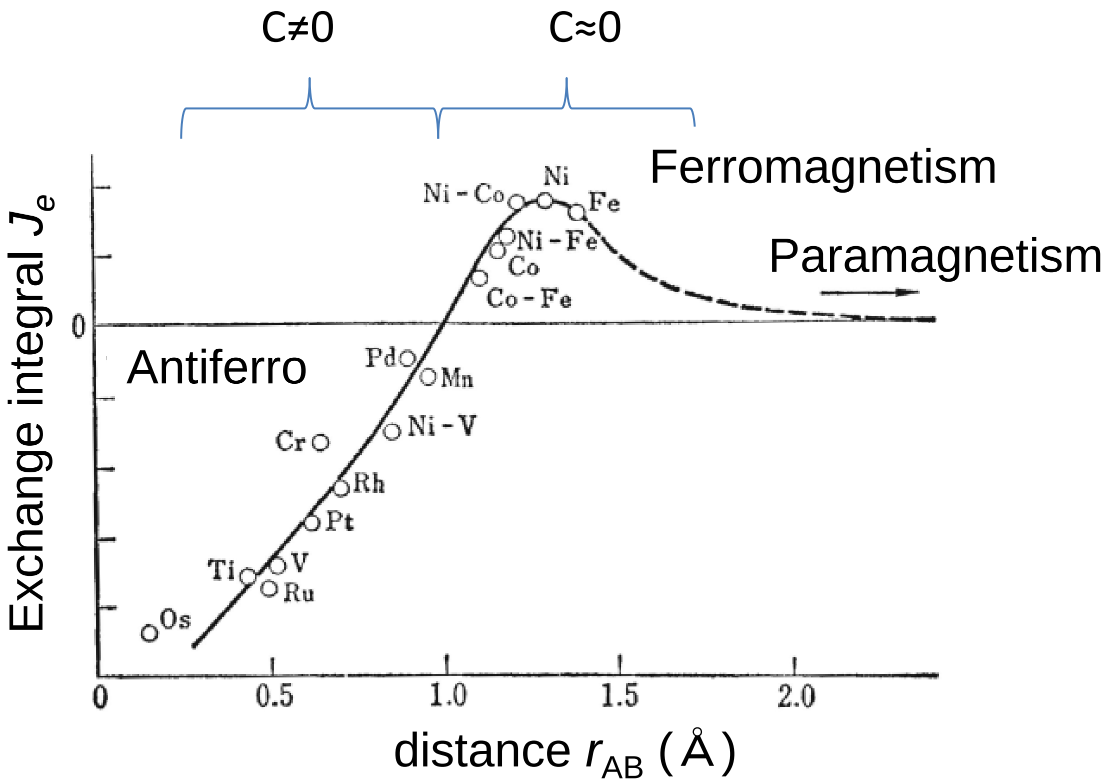
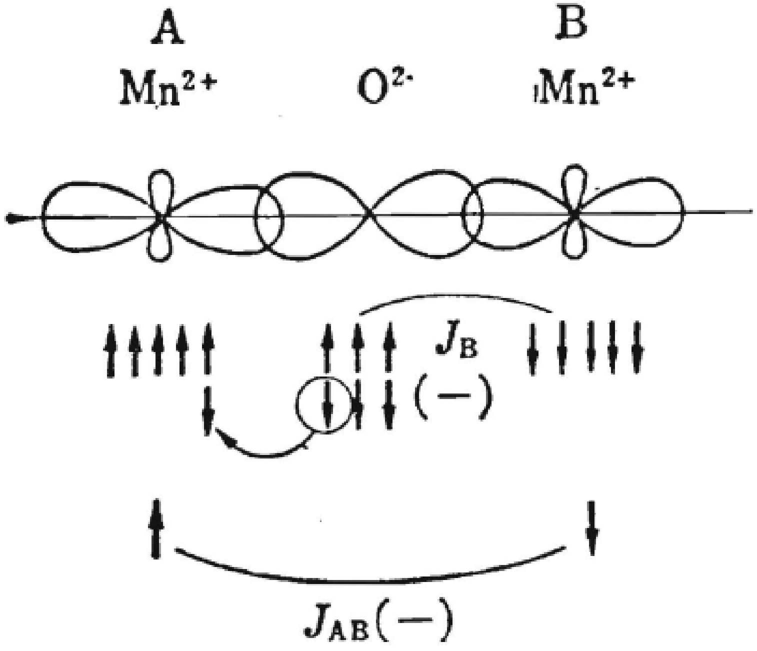
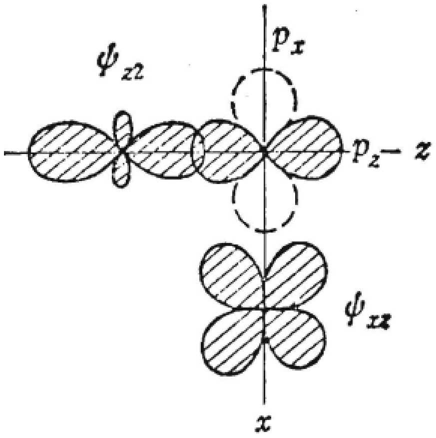
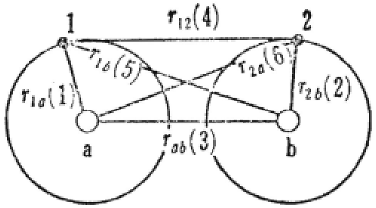
Review







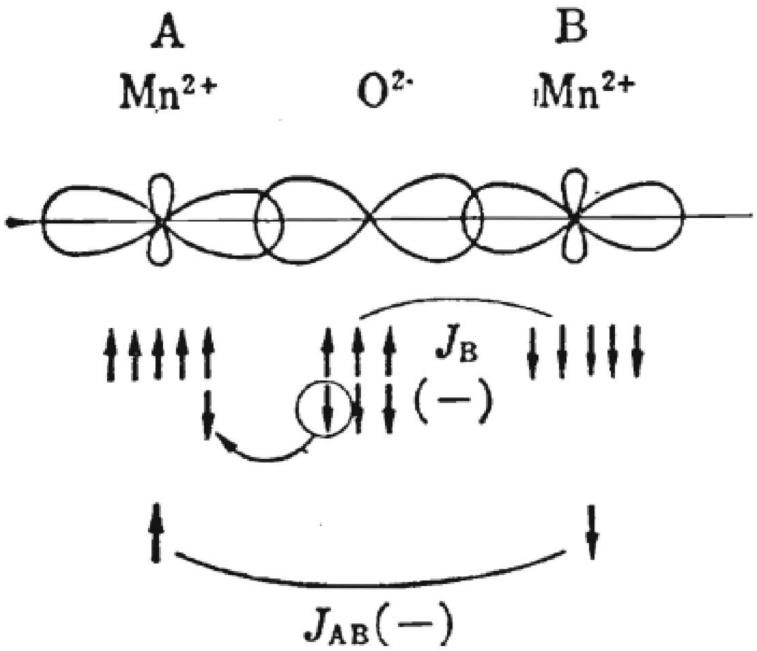


$$H_{total} = -\frac{h^2}{2m}(\nabla_1{}^2 + \nabla_2{}^2) + \frac{1}{4\pi\varepsilon_0}\left(\frac{-e^2}{r_{1a}} + \frac{-e^2}{r_{2b}}\right) + \frac{1}{4\pi\varepsilon_0}\left[\frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} + \frac{-e^2}{r_{1b}} + \frac{-e^2}{r_{2a}}\right]$$

$$J_e = J_0 - 2C_{ab}V_{ab}$$

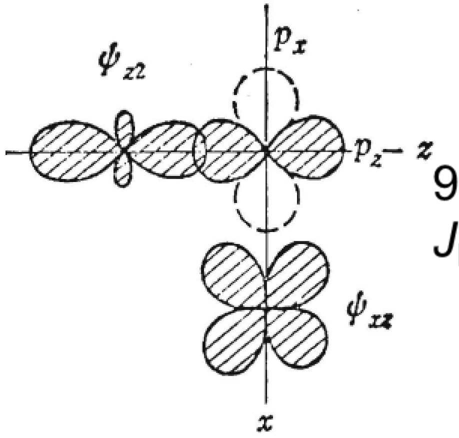
Super-exchange interaction

Review



MnO: Anti-Ferromagnetism
Mn^{2+}: d^5 configuration

1. *p* electron is transferred to atom A. Sign depends on d number in A.
2. Exchange interaction between oxygen and atom B. J_B depends on hybridization.
3. J_{AB} can be estimated by 3rd order perturbation.



90° case
J_B is π bonding.

Goodenough-Kanmori rule
Progr. Theoret. Phys. **30**, 275-89 (1963).

A-B	180°	90°
d^3-d^3	AF (weak)	AF or F
d^5-d^5	AF	AF (weak)
d^8-d^8	AF (strong)	F
d^3-d^8	AF (weak)	AF or F
d^5-d^8	AF (strong)	F (weak)
d^3-d^5	F (weak)	AF (weak)

Q5: Summarize about superexchange interaction.

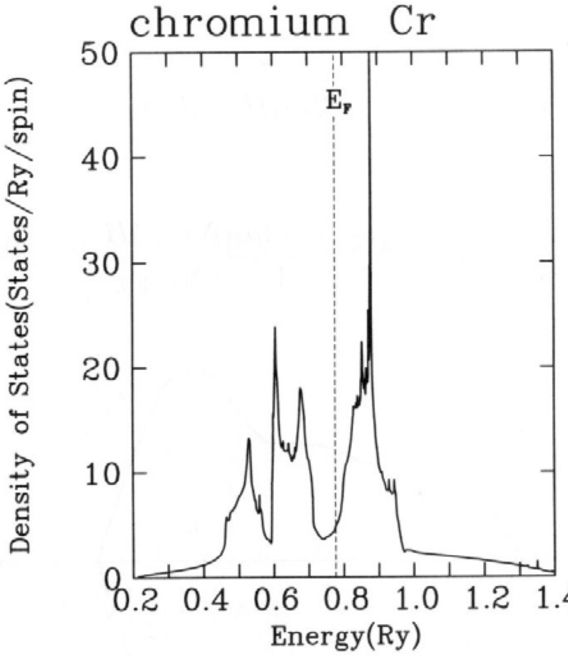
Band structures of transition metals

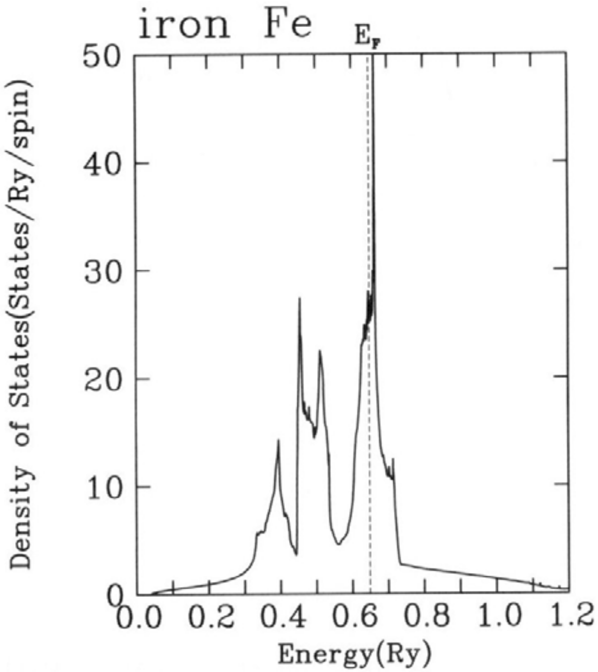
Review

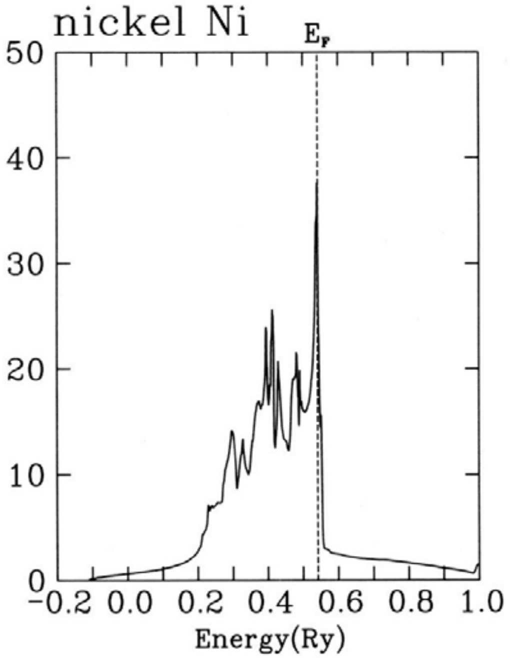
LDA calculation $$\left[-\frac{1}{2}\Delta_i-\frac{Z}{r_i}+\int\rho(r_j)\frac{1}{r_{ij}}d\boldsymbol{r}_j-\left(\frac{3}{\pi}\rho(r_i)\right)^{1/3}\right]\psi_\lambda(\boldsymbol{r}_i)=E_\lambda\psi_\lambda(\boldsymbol{r}_i)$$

Not ferromagnetic

Ferromagnetic

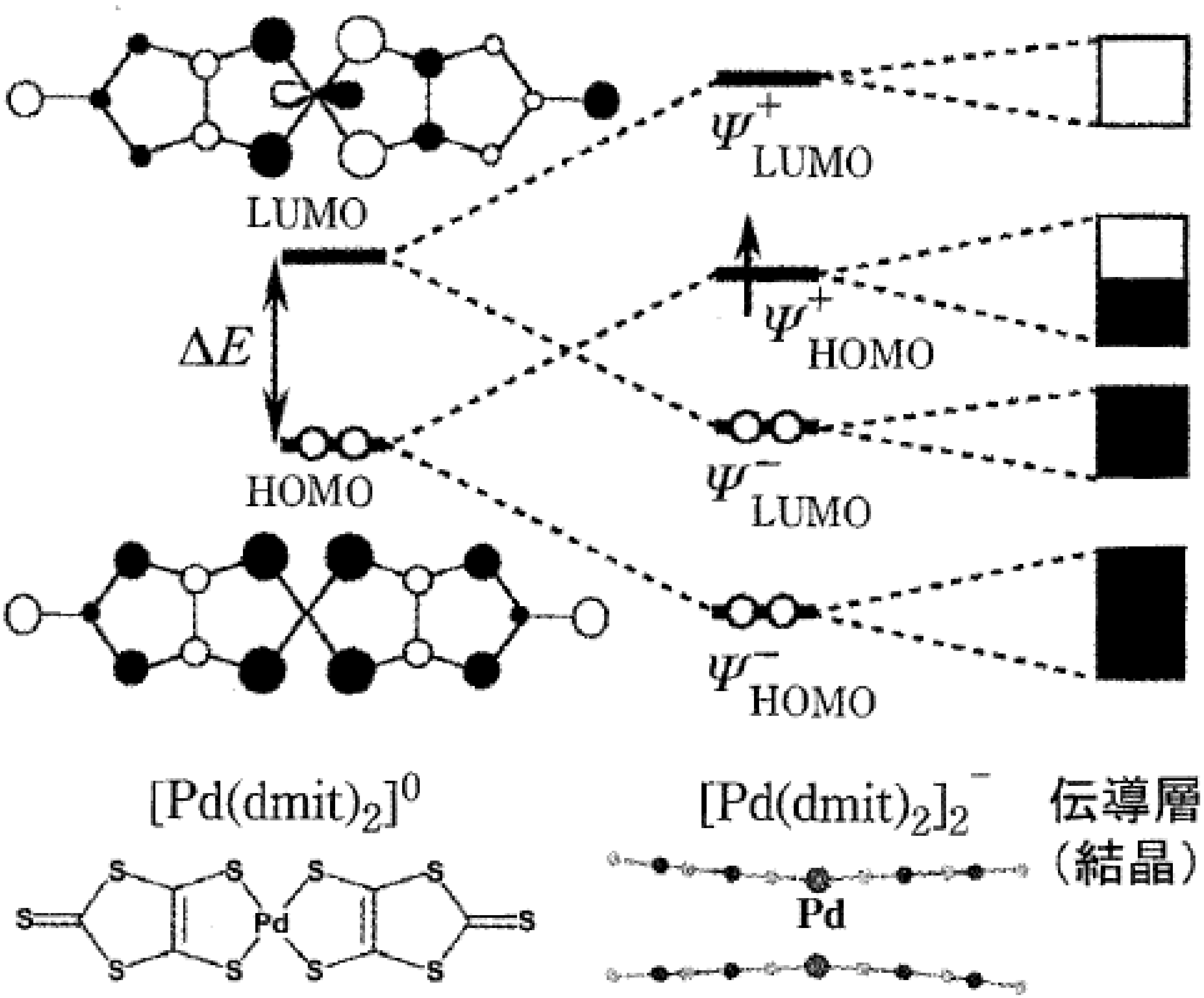






E_F position changes with increasing electron filling. (**Rigid band** picture)

From molecular orbitals to band structures



Ligand-field theory

Coulomb interaction vs. Ligand field energy 10Dq

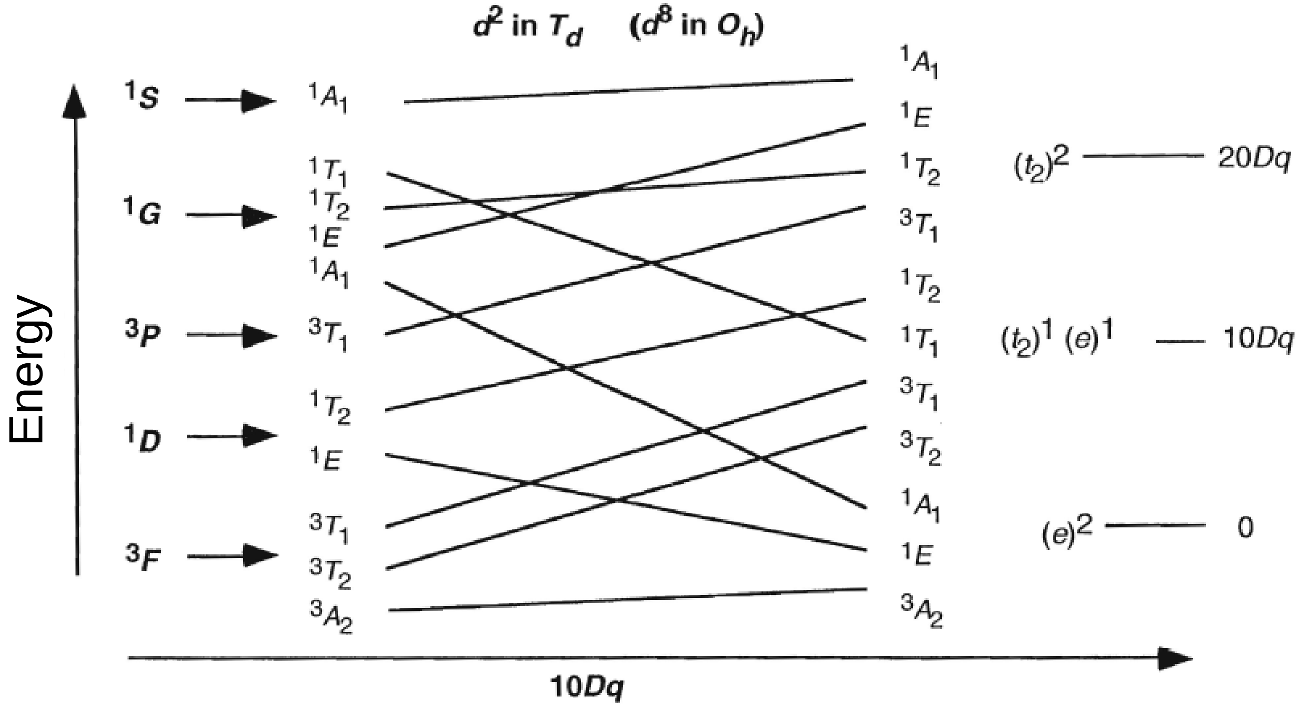
$$H = H_0 + H_{\text{Repulsion}} + H_{\text{SO}} + H_{\text{Ligands}}$$

$$= \sum_i \left(-\frac{\hbar^2 \nabla_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{r_{ij}} + \lambda \vec{L} \cdot \vec{S} + \sum_n \frac{z_n e^2}{r_n}$$

Hund's rule
Maximum S states are stable.
Maximum L states are stable.
d^2case: ${}_{10}C_2=45$, ${}^3F<{}^1D<{}^3P<{}^1G<{}^1S$

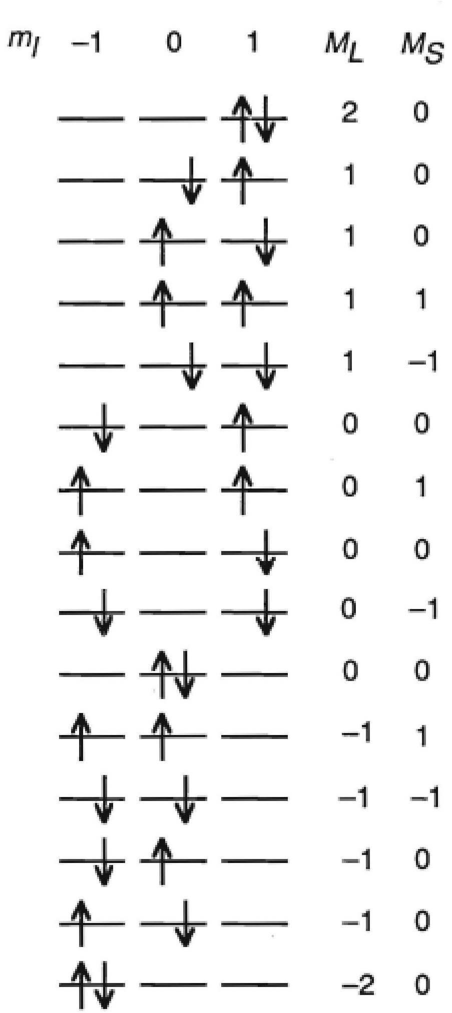
$H_{\text{Repulsion}} > H_{\text{Ligands}} > H_{\text{SO}}$
Weak field

$H_{\text{Ligands}} > H_{\text{Repulsion}} > H_{\text{SO}}$
Strong field



Q11: Describe 45 cases in d^2 configuration with term symbol.

Term symbol $^{2S+1}L_J$



m_l	−1	0	1	M_L	M_S
			↑↓	2	0
		↓	↑	1	0
		↑	↓	1	0
		↑	↑	1	1
		↓	↓	1	−1
	↓		↑	0	0
	↑		↑	0	1
	↑		↓	0	0
	↓		↓	0	−1
		↑↓		0	0
	↑	↑		−1	1
	↓	↓		−1	−1
	↓	↑		−1	0
	↑	↓		−1	0
	↑↓			−2	0

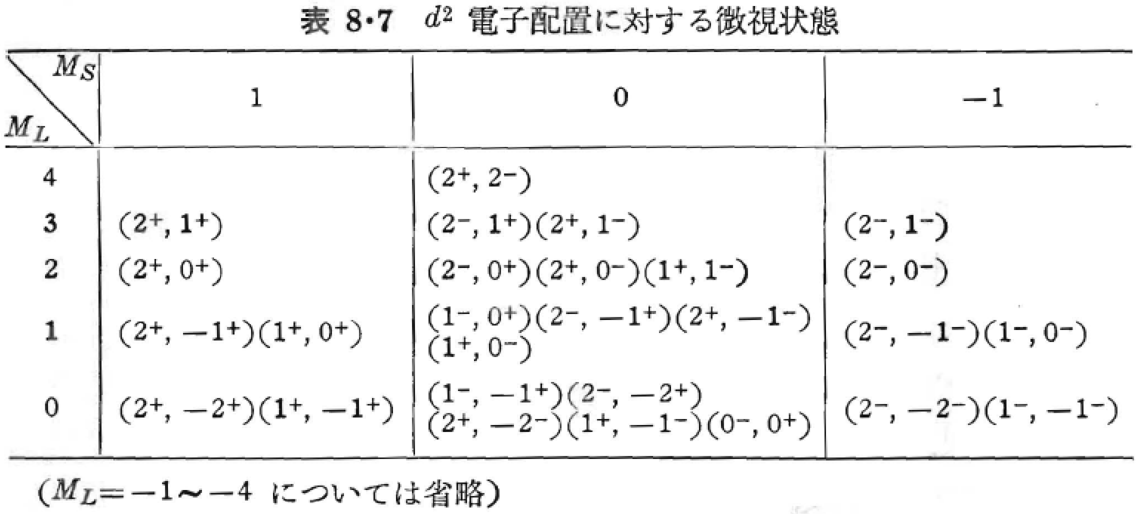
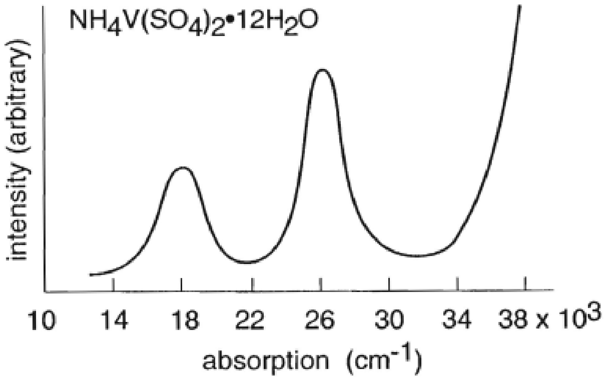


表 8·7　d^2 電子配置に対する微視状態

M_L \ M_S	1	0	−1
4		$(2^+, 2^-)$	
3	$(2^+, 1^+)$	$(2^-, 1^+)(2^+, 1^-)$	$(2^-, 1^-)$
2	$(2^+, 0^+)$	$(2^-, 0^+)(2^+, 0^-)(1^+, 1^-)$	$(2^-, 0^-)$
1	$(2^+, -1^+)(1^+, 0^+)$	$(1^-, 0^+)(2^-, -1^+)(2^+, -1^-)$ $(1^+, 0^-)$	$(2^-, -1^-)(1^-, 0^-)$
0	$(2^+, -2^+)(1^+, -1^+)$	$(1^-, -1^+)(2^-, -2^+)$ $(2^+, -2^-)(1^+, -1^-)(0^-, 0^+)$	$(2^-, -2^-)(1^-, -1^-)$

($M_L = -1 \sim -4$ については省略)

Tanabe-Sugano (田辺 - 菅野) diagram



ε_1 →

ε_2 →

$\varepsilon_2 / \varepsilon_1 = 1.5$

(1cm⁻¹ = 0.124meV)

Analysis of absorption spectrum
to deduce Coulomb interaction and ligand field strength
from multiplet calculation

1. Estimate energy peak ratio E1/E2.
2. Find the *Dq* position using TS diagram.

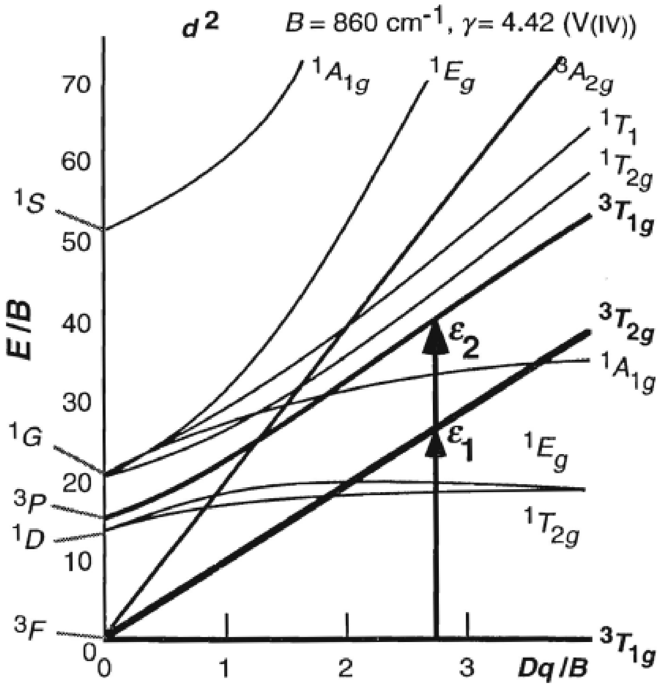
$$\varepsilon_1 \;:\; {}^3T_{1g} \;\rightarrow\; {}^3T_{2g},$$
$$\varepsilon_2 \;:\; {}^3T_{1g} \;\rightarrow\; {}^3T_{1g} \qquad \rightarrow \qquad Dq = 2.8\ B$$

3. Estimate the energies from diagram.

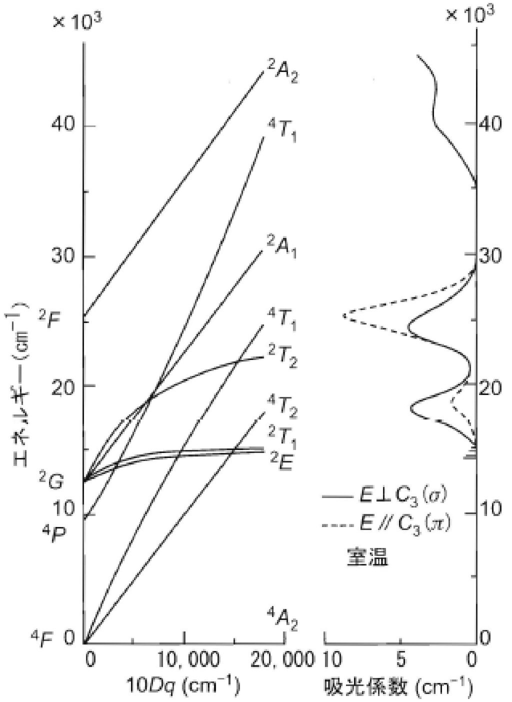
$$\varepsilon_1/B = 25.9 = 17200\ (\mathrm{cm}^{-1})/B \quad \rightarrow \quad B = 665\ \mathrm{cm}^{-1}$$

4. Calculate *Dq*.

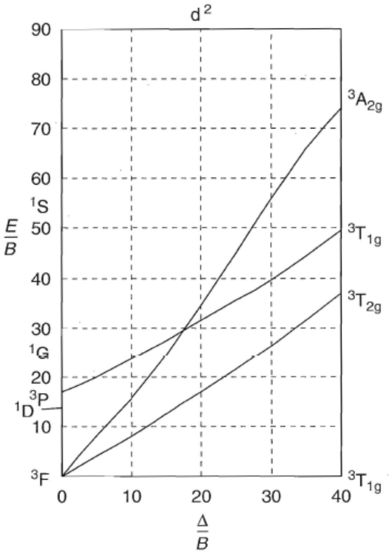
$$Dq = 2.8\ B = 1860\ \mathrm{cm}^{-1}$$

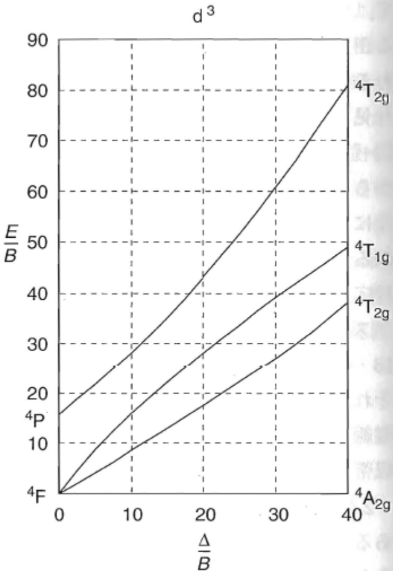


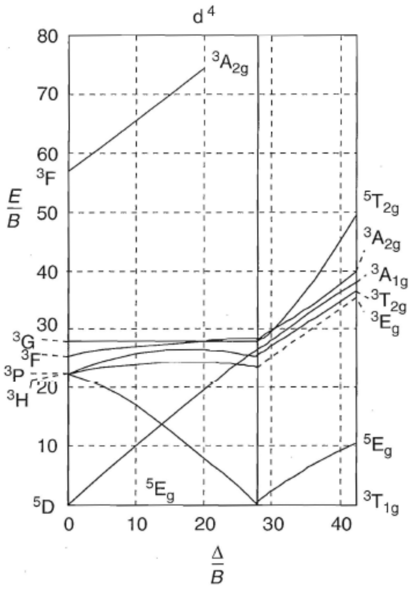
Tanabe and Sugano, J. Phys. Soc. Jap. 9, 766 (1954).

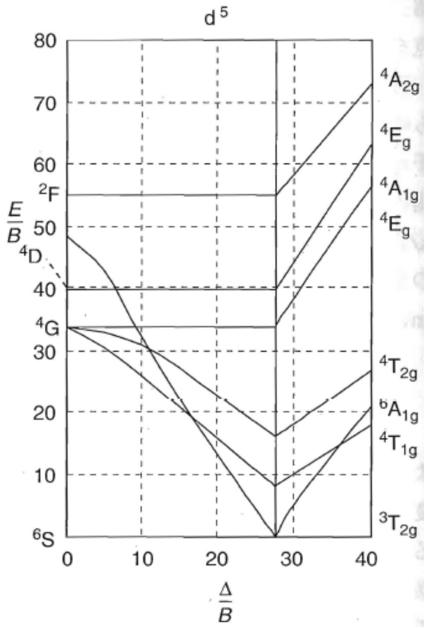


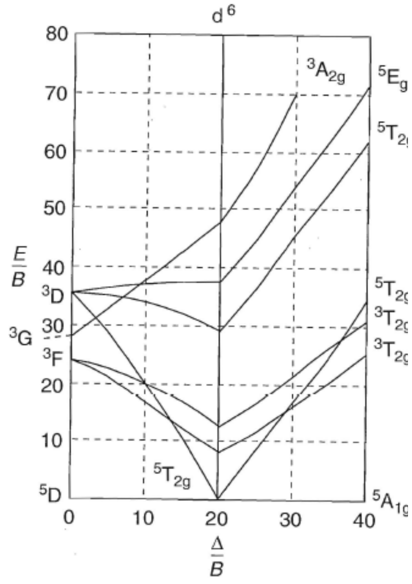
Tanabe-Sugano diagrams for $d^2 - d^8$

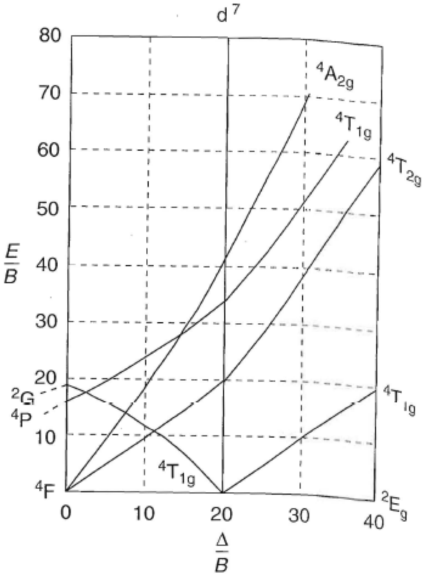


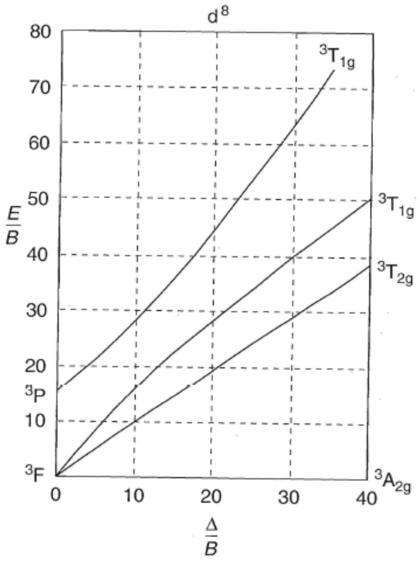












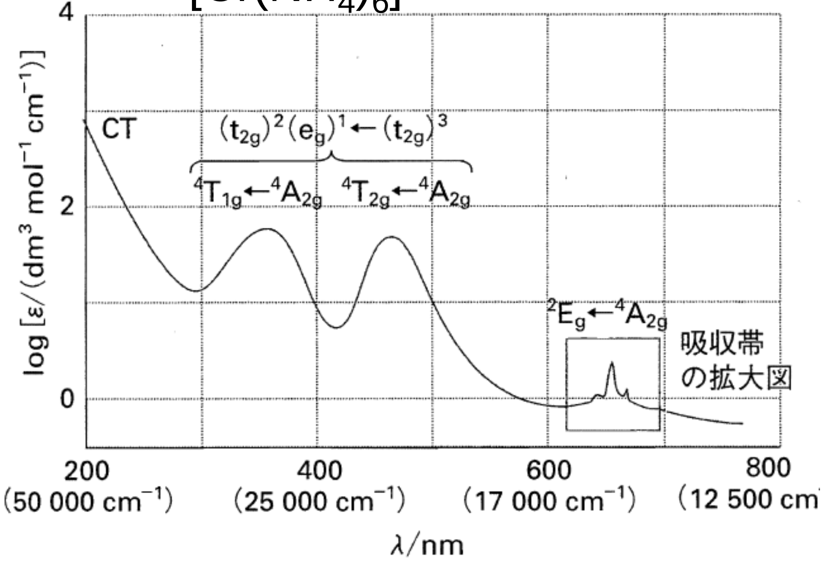
B: Racah parameter (Coulomb)

Δ: ligand field strength

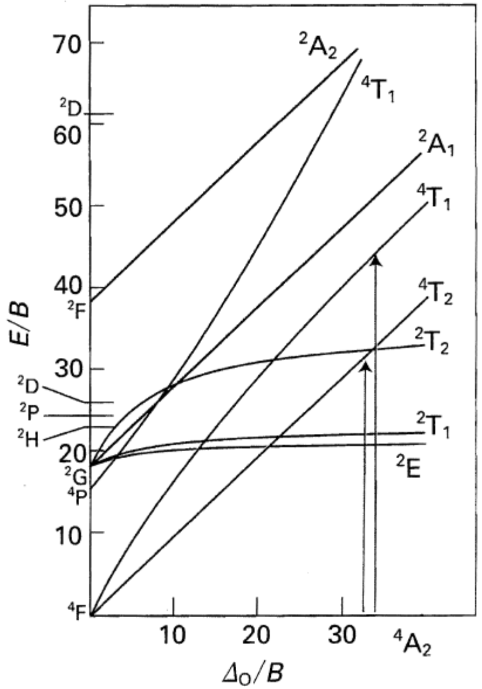
Tanabe and Sugano, J. Phys. Soc. Jap. 9, 766 (1954).

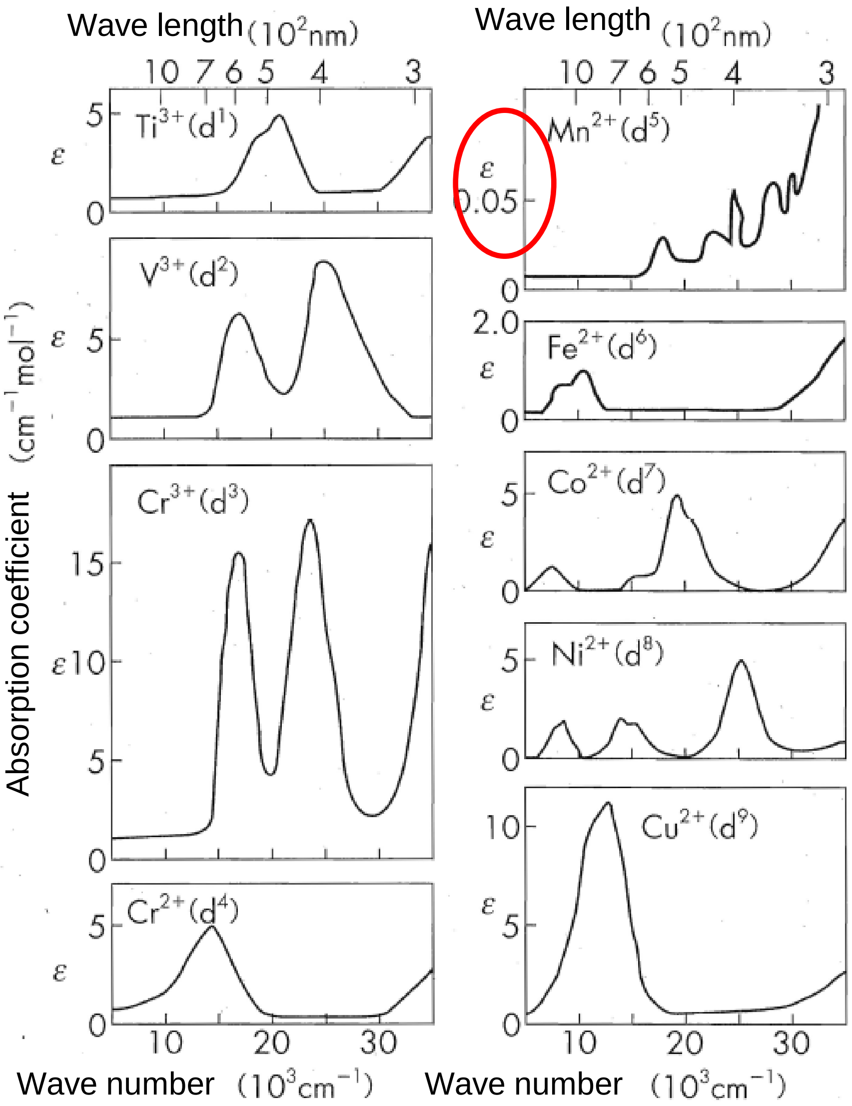
Ligand field theory

$[Cr(NH_4)_6]^+$



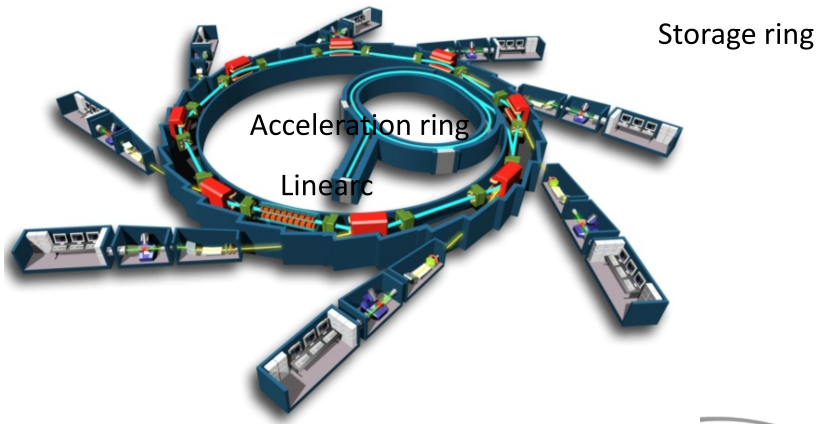
TS diagram for d^3 system



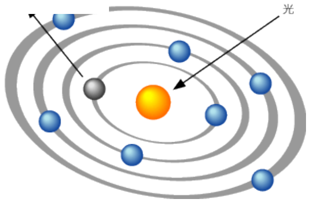


Q12: Estimate Racah parameter *B* and ligand field splitting *Δ*.

What is synchrotron radiation ?



http://en.wikipedia.org/wiki/Synchrotron_light_source



KEK Photon Factory

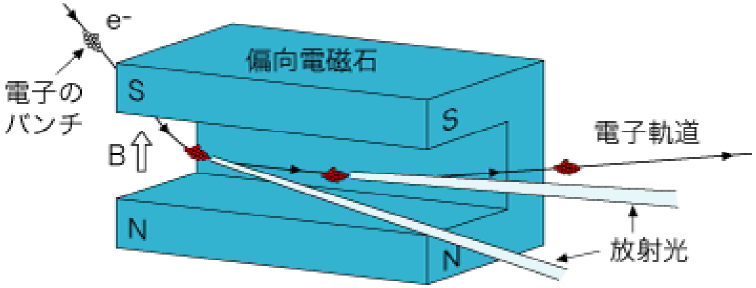
SPring-8

Synchrotron radiation

Bright

Polarized

Tunable photon energy



Electron beam orbits are bent by magnetic field.

⇩

Generation of synchrotron radiation

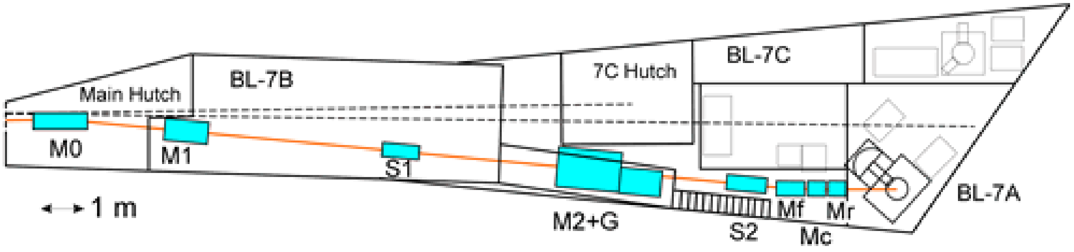
Q13: Summarize the principle of synchrotron radiation.

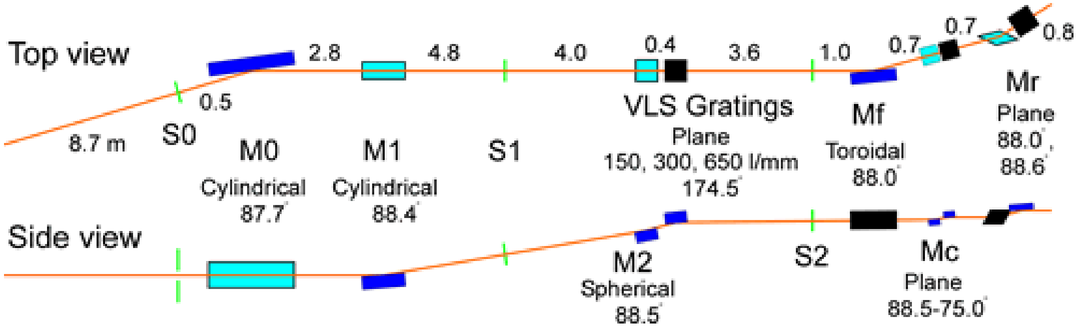
Research Center for Spectrochemistry (RCS), The University of Tokyo

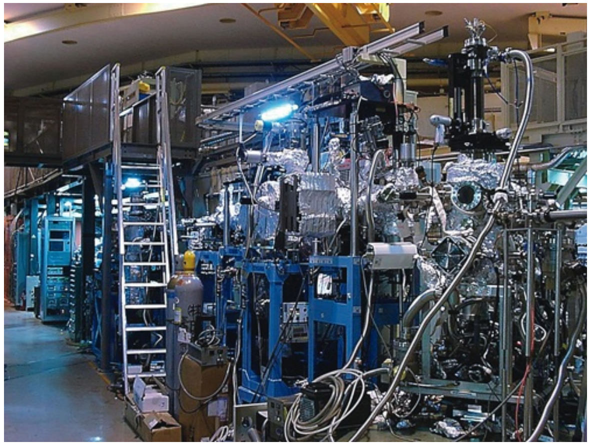
RCS has a beam line at Photon Factory in KEK.

BL-7A: Bending magnet is used. Energy ranges of hv=50-1300 eV are obtained.

Suitable for K-edge absorption for C, N, and O, L-edge absorption for transition metals, and high-resolution core-level photoemission spectroscopy



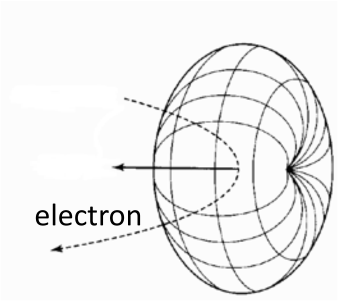




Synchrotron Radiation

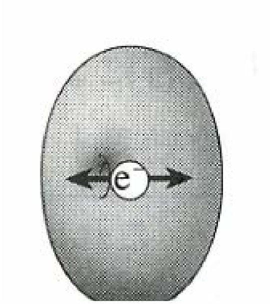
Synchrotron radiation derived from the ‘relativity theory’.

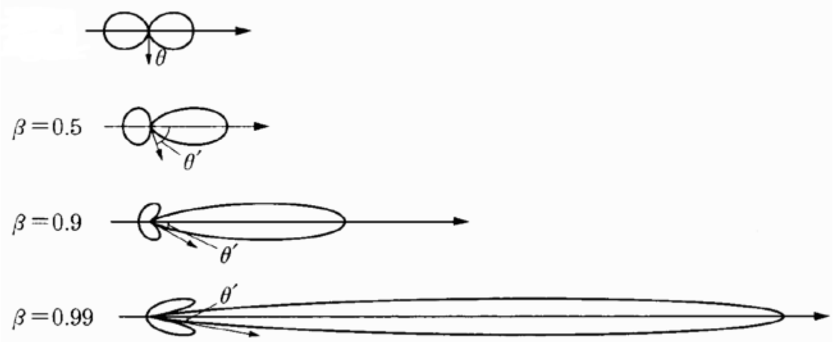
Radiation theory $$\frac{dP}{d\Omega} \propto \left|\frac{d^2 r}{dt^2}\right|^2 \sin^2\theta \qquad \gamma = \frac{E}{mc^2} = \frac{1}{\sqrt{1-\beta^2}} = 1957E \quad \text{[GeV]}$$

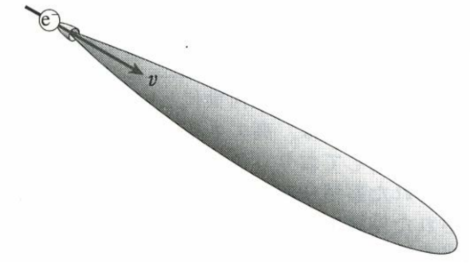


Lorentz transformation

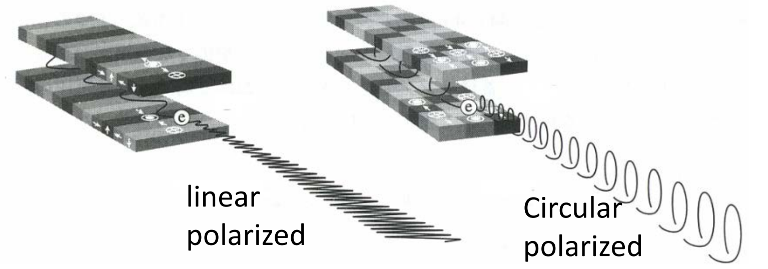
$$\tan\theta' = \frac{1}{\gamma}\frac{\sin\theta}{\cos\theta + \beta}$$







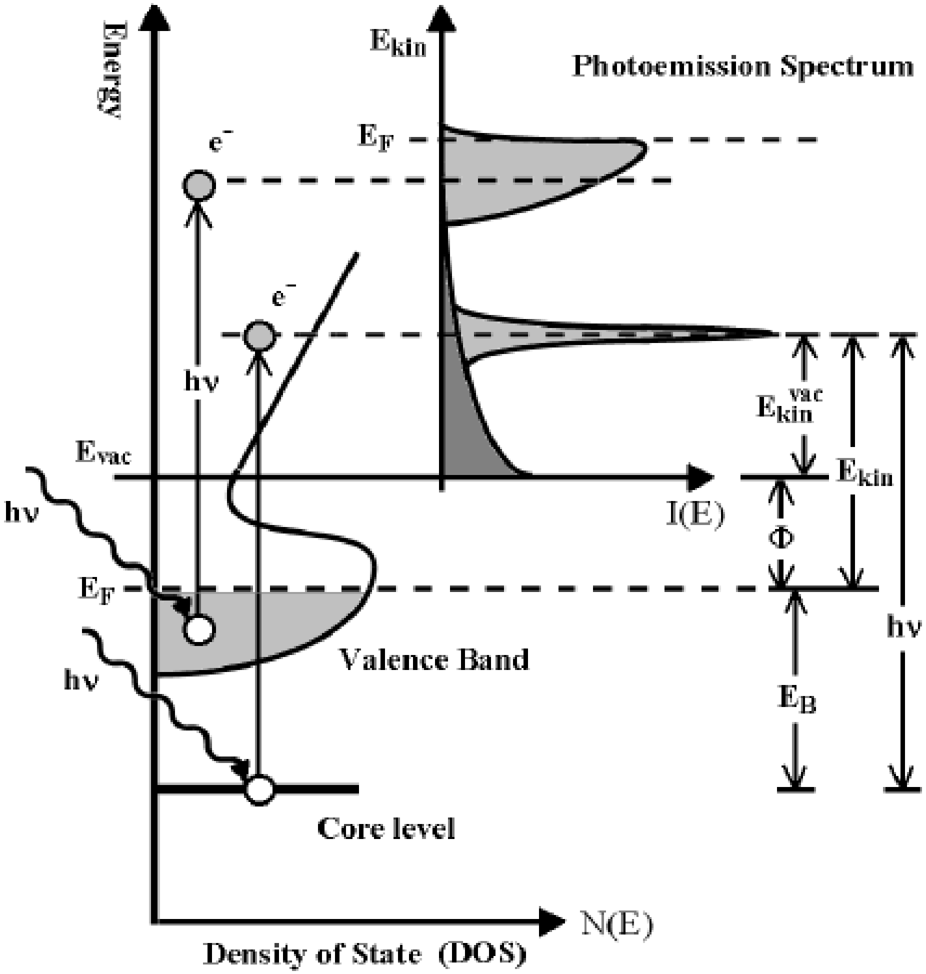
Undulator



1 GeV -> β=99.99999 % -> broadening 1/γ

8 GeV -> γ=15660, 0.1 mrad

Principle of photoemission spectroscopy



$$h\nu = E_B + E_{kin.} + \phi$$

E_B; Binding energy

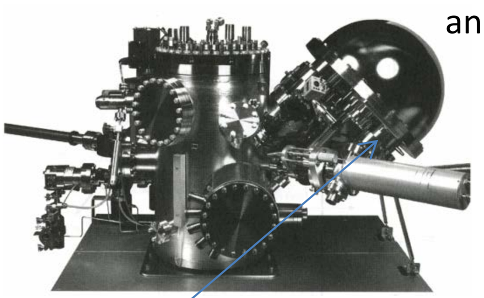
$E_{kin.}$; Kinetic energy of photoelectron

ϕ; Work function （Energy difference between Fermi level and vacuum level)

Photoemission spectroscopy ; Electrons with various kinetic energies are collected.

Density of states (DOS)
Band structures
Energy of molecular orbital

X-ray photoemission spectroscopy (XPS)



Mg kα hv=1253.6 eV
Al kα hv=1486.6 eV

Magnetically shielding in chamber
(earth: 350 × 10^{-7} Tesla)

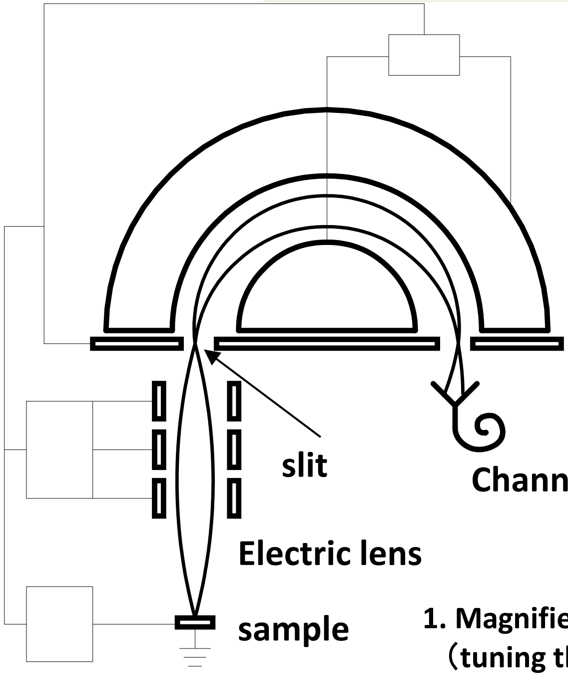
For valence-band measurements,
He sources (hv=21.2 eV, and 40.8 eV) are used.

Fermi's Golden rule

$$I(\omega) \propto \sum_k \left|\left\langle \Psi_n^{N-1} | a_k | \Psi_n^{N-1} \right\rangle\right|^2 \delta(\omega-(E_0^N - E_n^{N-1}+\mu))$$

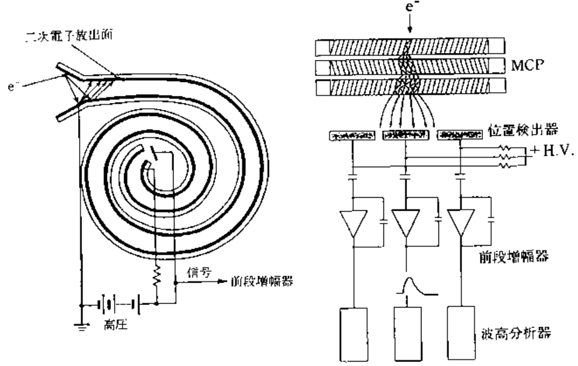
Matrix element　　DOS

$|\Psi_0^N>$: initial state
$|\Psi_0^{N-1}>$: final state
a : dipole moment



1. **Magnified by the electric lens (tuning the detection area)**
2. **Electron velocity is related to the pass energy.**
3. **Electrons possessing the pass energy pass the analyzer.**
4. **Electron counts are detected by Channeltron.**

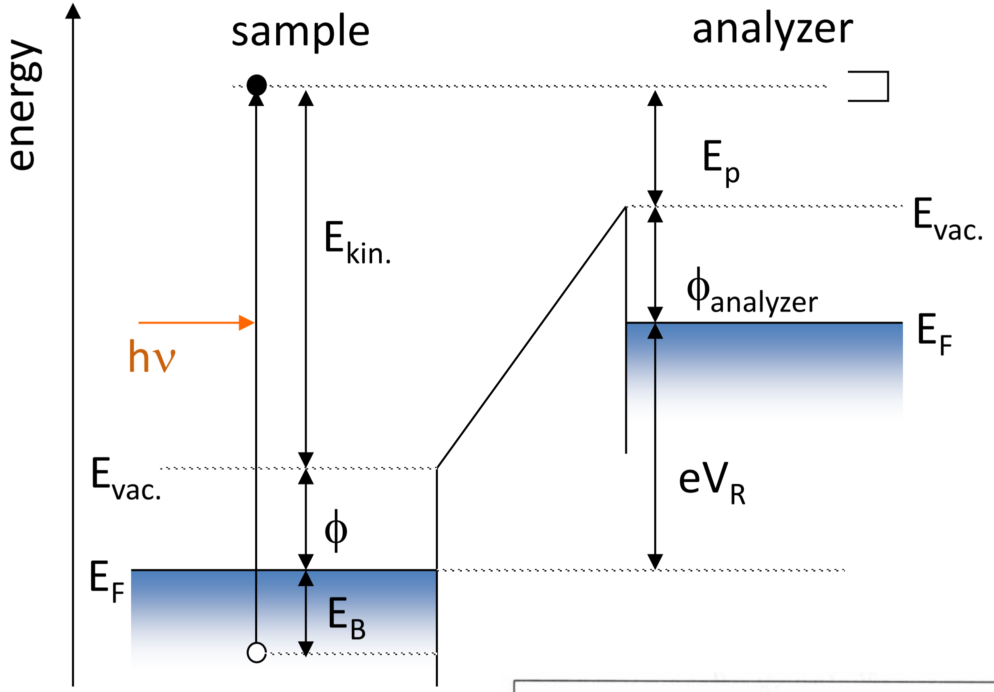
Principles of channeltron



The counts of secondary electrons are enhanced.

Q14: Prove the Fermi's golden rule.

Energy diagram in photoemission spectroscopy



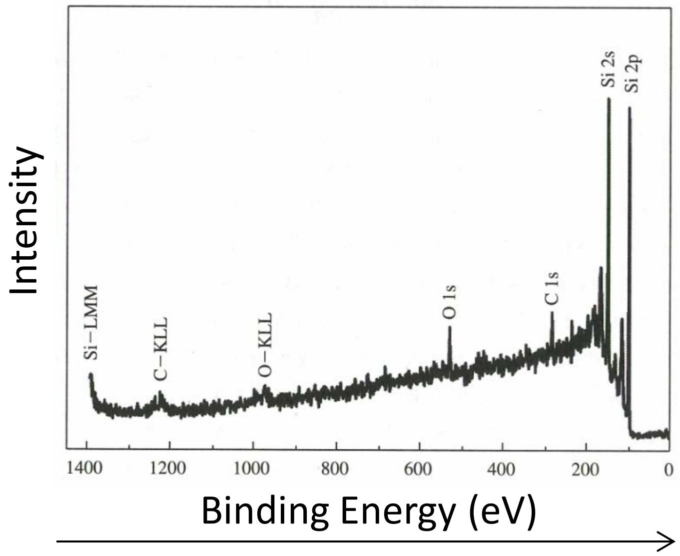
Energy conservation

$$h\nu = E_B + E_{kin.} + \phi$$

$$E_p + eV_R + \phi_a = E_{kin.} + \phi_s$$

Φ_a depends on the instrument condition (baking).

Energy calibration is required.



Kinetic Energy

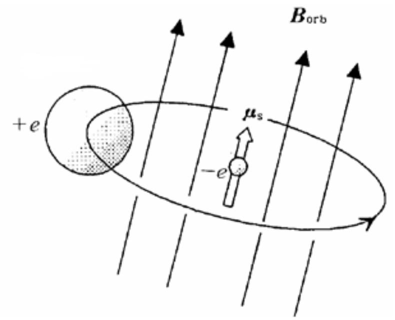
Spin-orbit interaction

Motion of electrons around the nucleus induce the magnetic field.
Spin-orbit interaction splits to two states of j=l+1/2, j=l-1/2.
Intensity ratio is l+1 : l , which is related to the degeneracy of 2j+1.

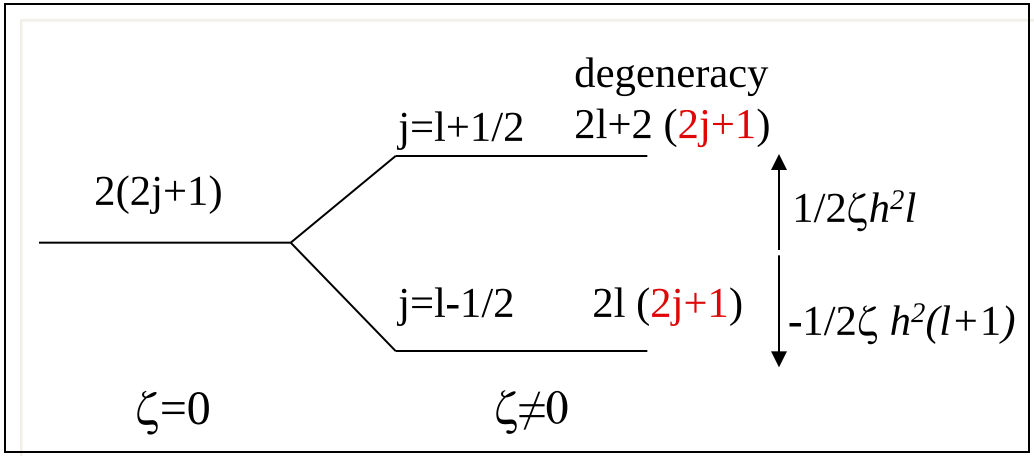
$$H_{SO}=\zeta(l\cdot s)=\zeta/2(j^2-l^2-s^2)$$

$$j=l+1/2;\ E(l+1/2)=1/2\ \zeta h^2 l$$

$$j=l-1/2;\ E(l-1/2)=-1/2\ \zeta h^2(l+1)$$



orbital	quantum number		ratio
	l	*j*	
s	0	1/2	
p	1	1/2	1
	1	3/2	2
d	2	3/2	2
	2	5/2	3
f	3	5/2	3
	3	7/2	4


degeneracy

j=l+1/2 2l+2 (2j+1)

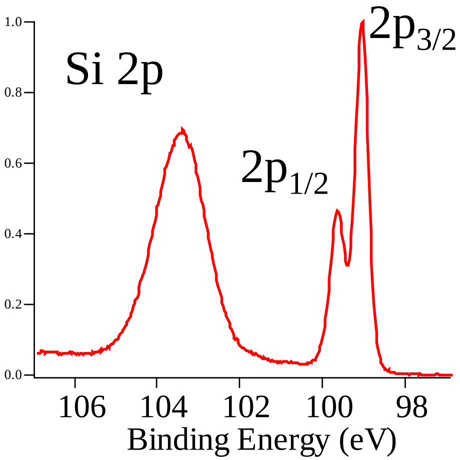
2(2j+1)

$1/2\zeta h^2 l$

j=l-1/2 2l (2j+1)

$-1/2\zeta\ h^2(l+1)$

$\zeta=0$ $\zeta\neq0$



Q15: Prove H_{SO} from Biot-Savart's law.

Q16: Prove H_{SO} from Dirac equation.

How quantum mechanics is modified ?

- Schrödinger equation (non-relativity)

$$\varepsilon = \frac{p^2}{2m} \longrightarrow i\hbar\frac{\partial\psi(r)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(r)$$

$$\boxed{\varepsilon \leftrightarrow i\hbar\frac{\partial}{\partial t} \quad p \leftrightarrow -i\hbar\nabla}$$

- Relativity formulation

$$(p_x{}^2 + p_y{}^2 + p_z{}^2) - (\frac{\varepsilon}{c})^2 = -m^2c^2 \longrightarrow \quad ?$$

$$\boxed{\varepsilon \leftrightarrow i\hbar\frac{\partial}{\partial t} \quad p \leftrightarrow -i\hbar\nabla}$$

spin

Chemical shift of core-level spectra

Origin of the chemical shift

$\Delta E_B = k\Delta q + \Delta V - \Delta E_R$

q : charge

$V = \Sigma q_j / R_j$:

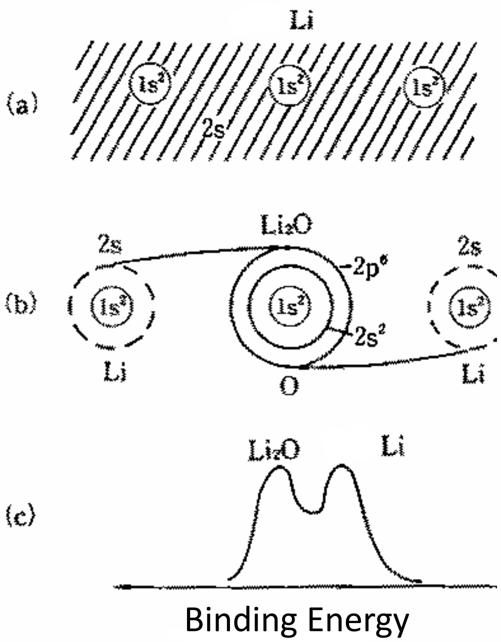
Madelung potential

(Sum of the static potentials)

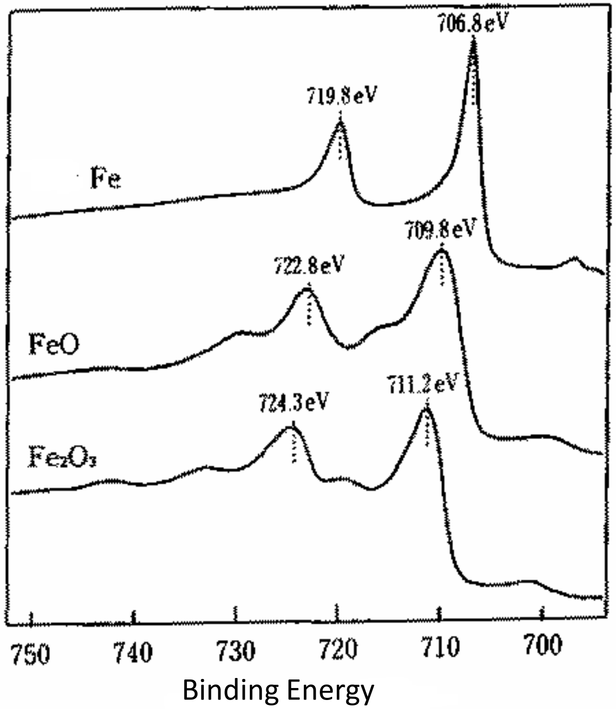
E_R : relaxation energy

(by core hole screening)

Li - Li_2O case



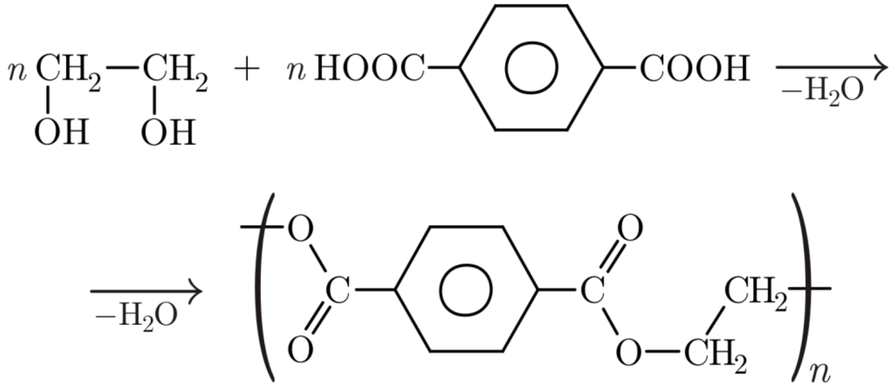
Fe compound cases

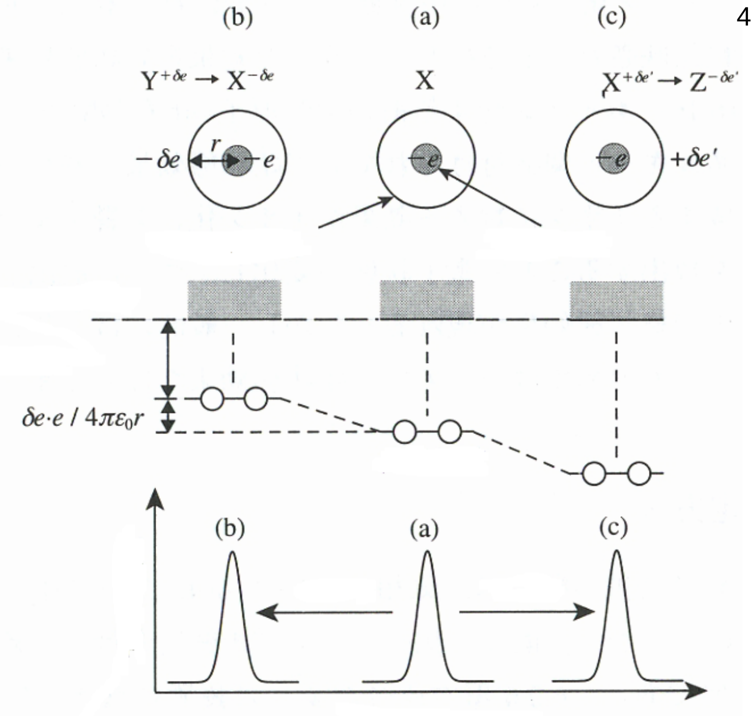


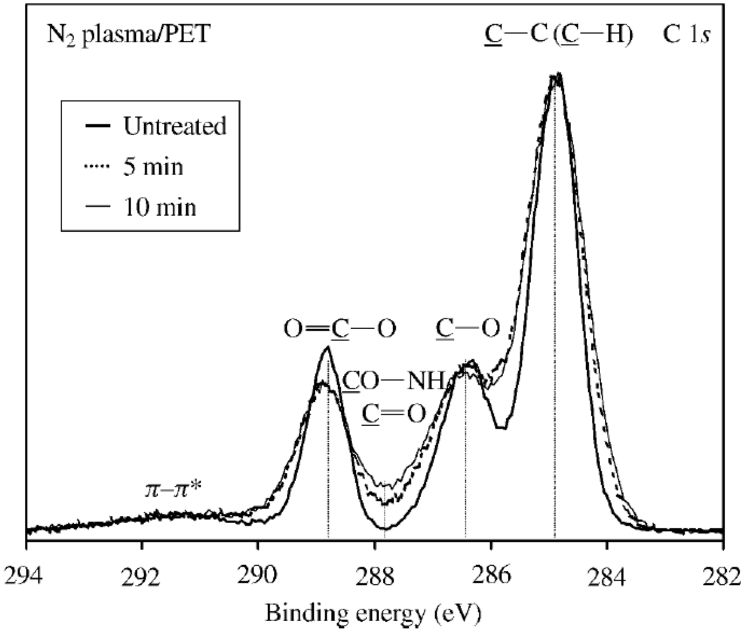
Peak position depends on the valence states, electron number, and the response in photoelectron emission. Therefore, the “chemical shift” gives us the information about the chemical bonding nature.

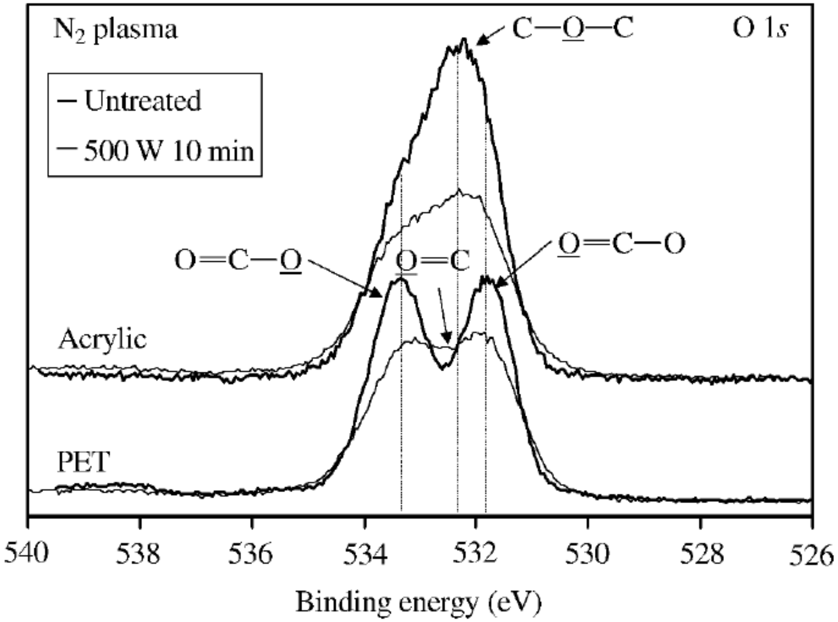
Q17: Summarize the principle of photoemission spectroscopy.

XPS of Polyethylene terephthalate (PET)









J. Adhesion Sci. Technol., Vol. 14, No. 12, pp. 1485–1498 (2000)

Chemical shifts in XPS

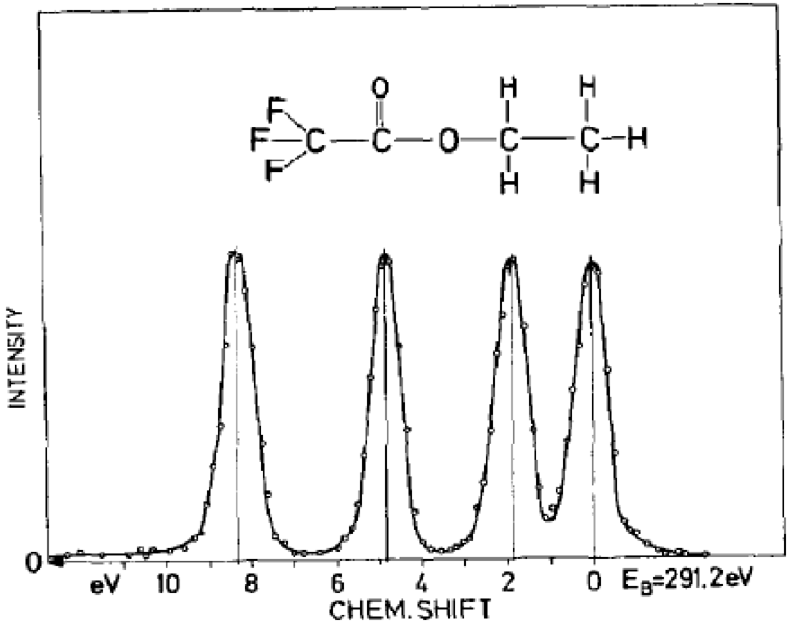


Figure 18. The carbon 1s electron lines in ethyl trifluoroacetate.

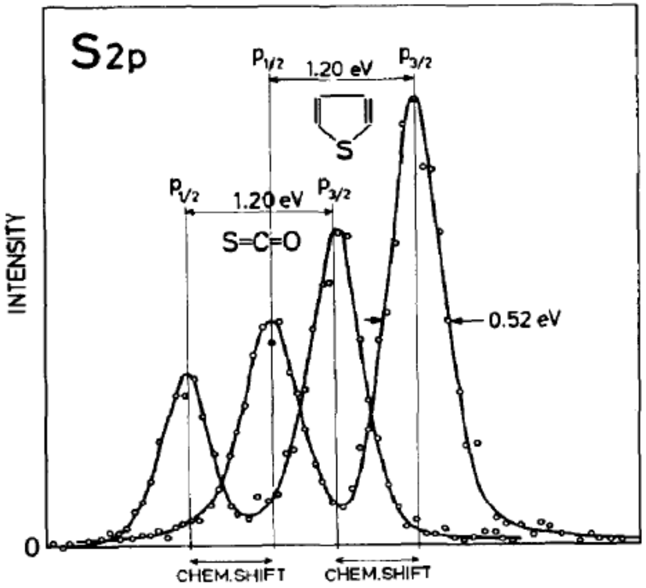


Figure 19. The superimposed sulphur 2p$_{1/2,\,3/2}$ lines from thiophene and carbonyl sulphide.

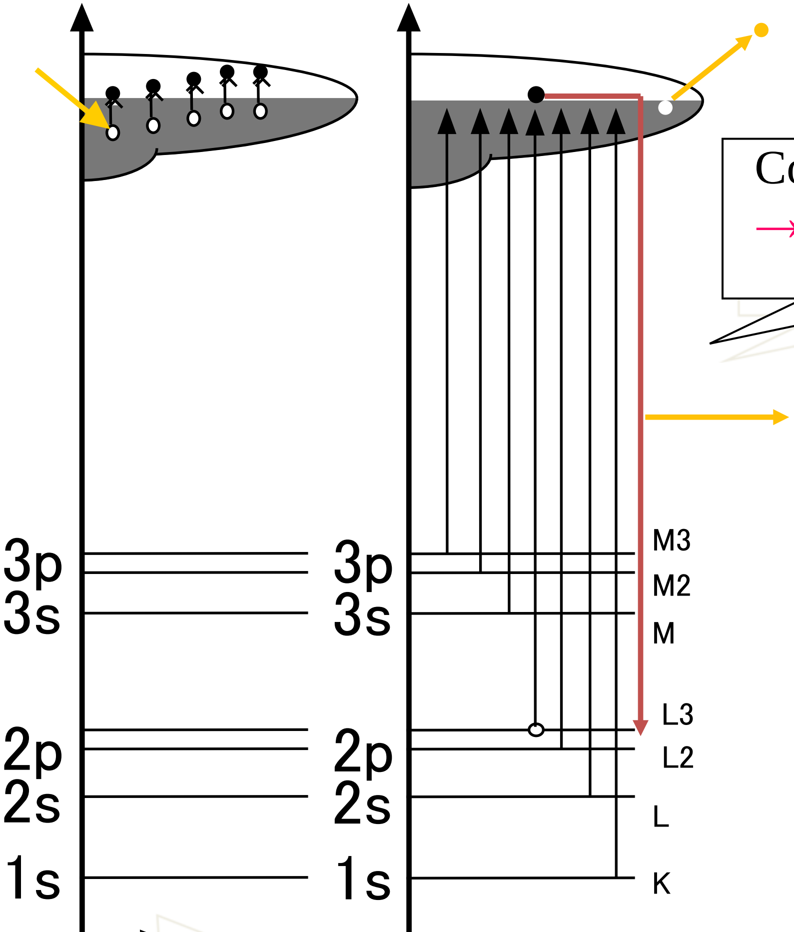
U. GELIUS, E. BASILIER, S. SVENSSON, T. BERGMARK and K. SIEGBAHN

Journal of Electron Spectroscopy and Related Phenomena, 2 (1974) 405–434

Q18: Explain the origin of chemical shift in XPS.

Q19: Draw the C 1s XPS line shape in CH_3COOCH_3 and CH_3-CHCl-CHI-CH_2-CH_3.

Core-level Absorption Spectroscopy

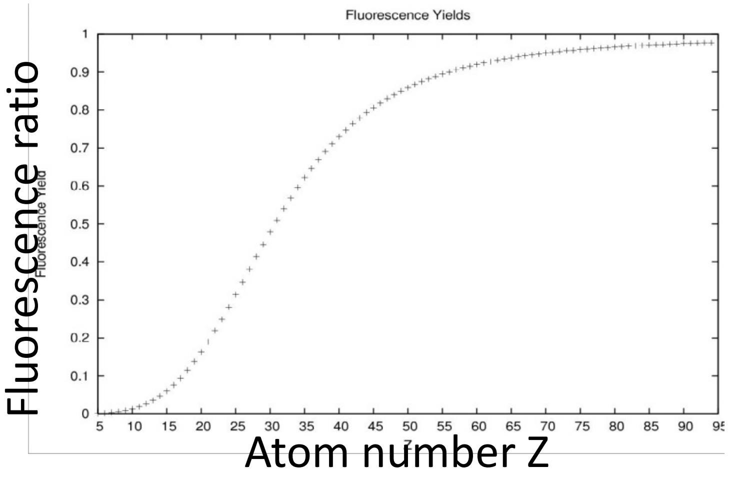


Auger electron (total electron yield)

Core-level transition
→ atomic information

Fluorescence yield

Auger electron spectroscopy
by constant kinetic energy

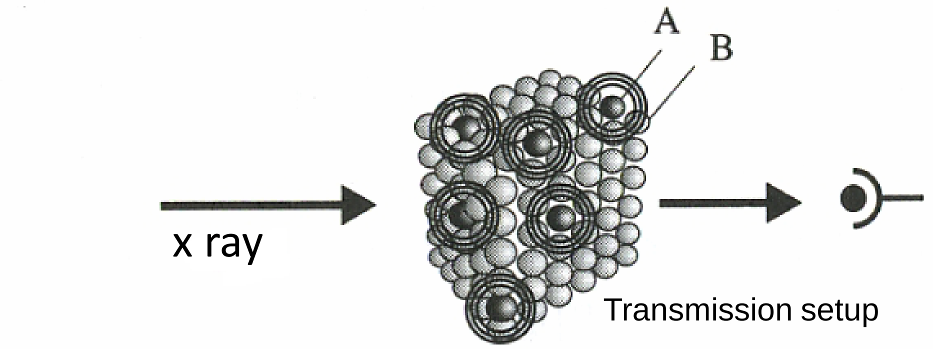


Interband transition
→ not neglecting
band dispersion

Q20: Explain the peak shift of Auger structure when changing photon energy.

X-ray Absorption Fine Structure (XAFS)

XAFS: X-ray absorption near-edge structure (XANES) and Extended XAFS (EXAFS)



Transmission setup

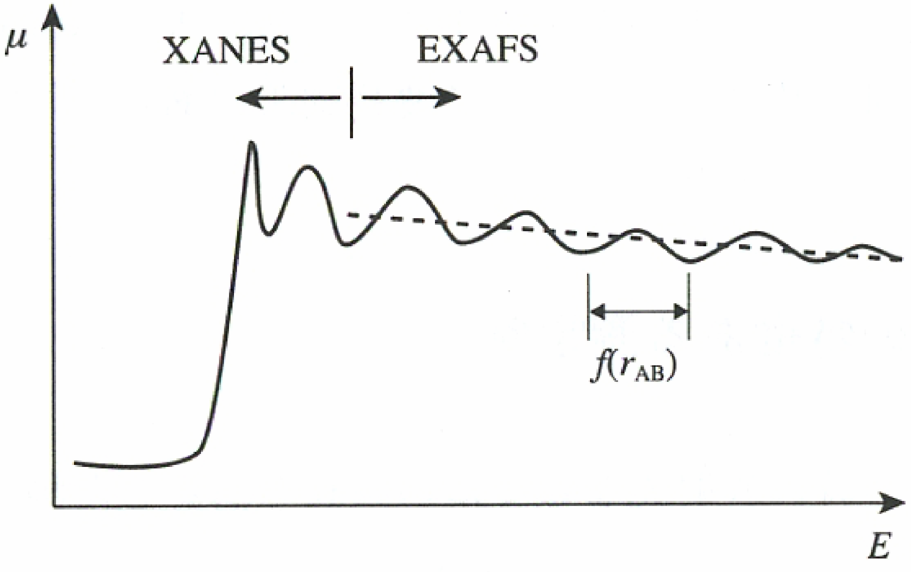
Interference between atoms

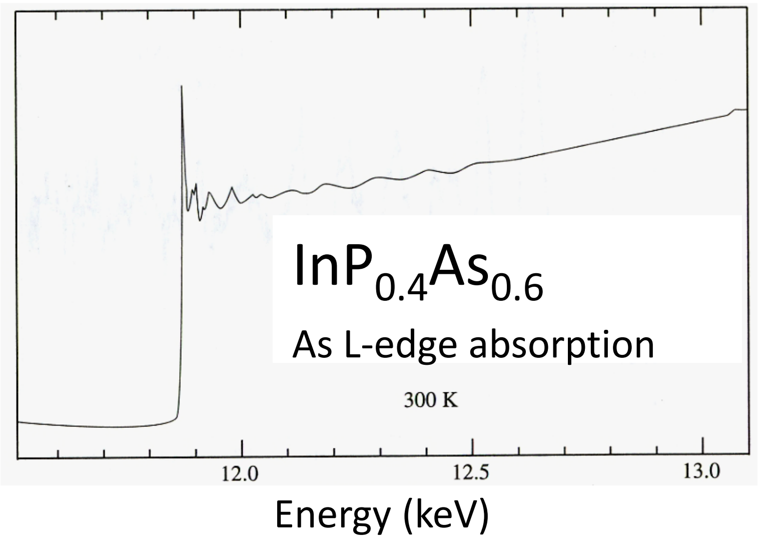
↓

Oscillation in absorption spectra

↓

Oscillation period depend on the lattice structure.

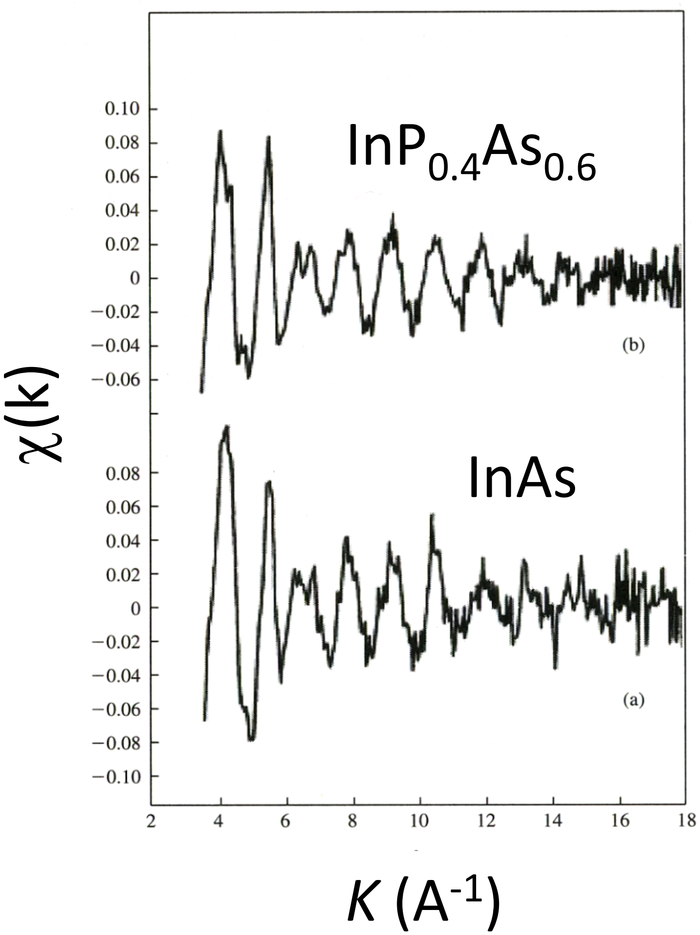


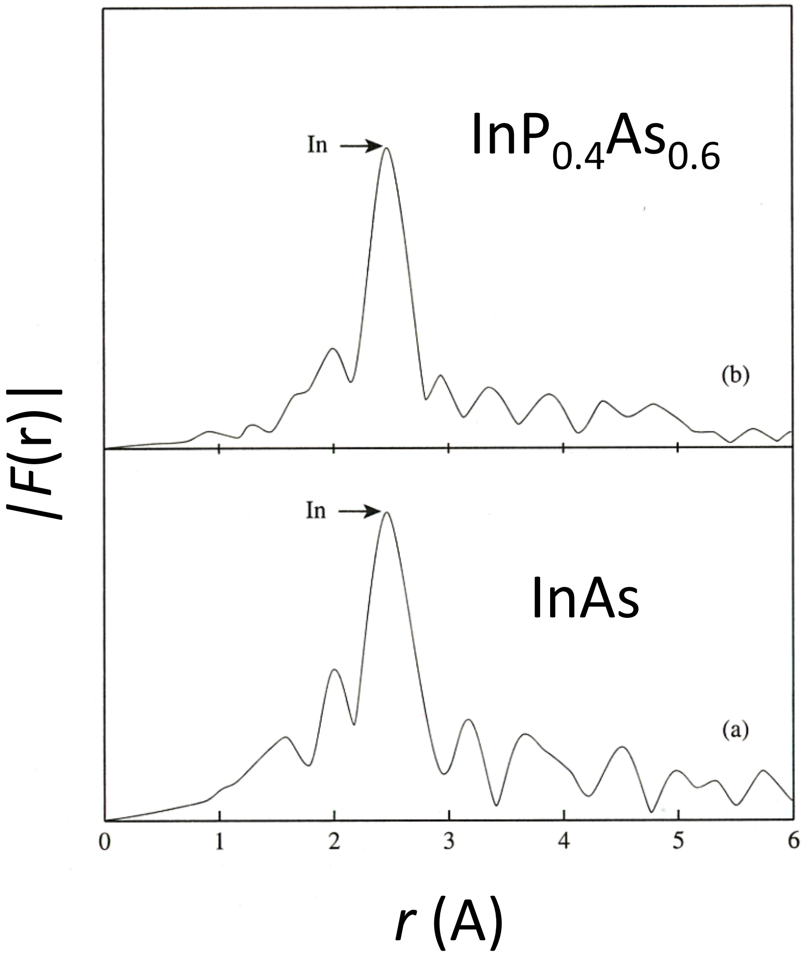


$InP_{0.4}As_{0.6}$

As L-edge absorption

EXAFS



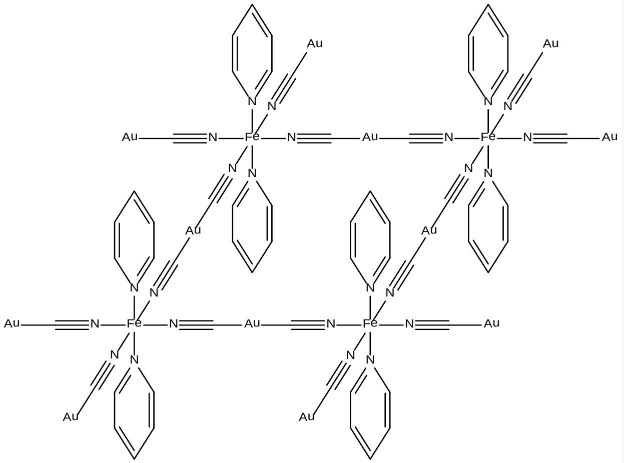


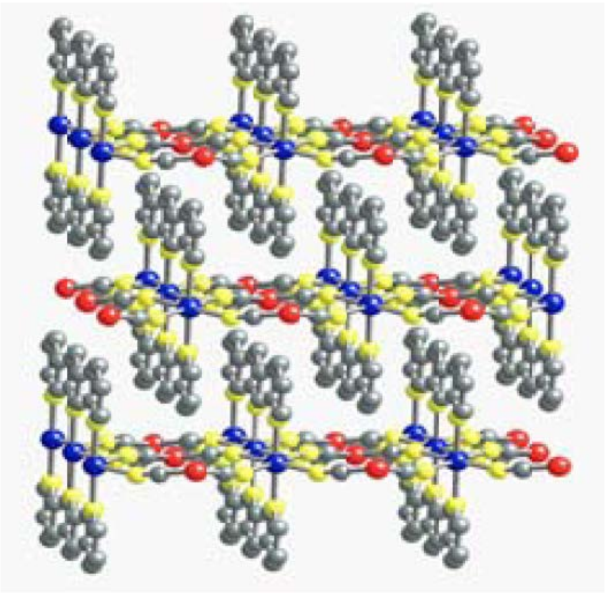
Fourier transformation

EXAFS reveals the nearest neighbor distance.

Y. Kuwahara et al. Jpn. J. Appl. Phys. **33**, 5631 (1994).

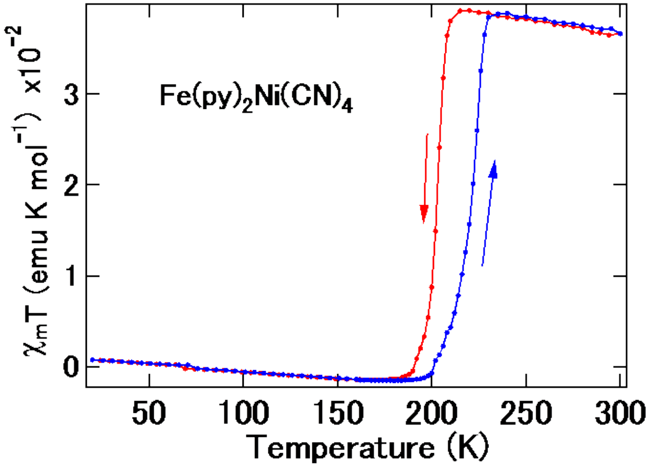
$Fe(py)_2Ni(CN)_4$ complex

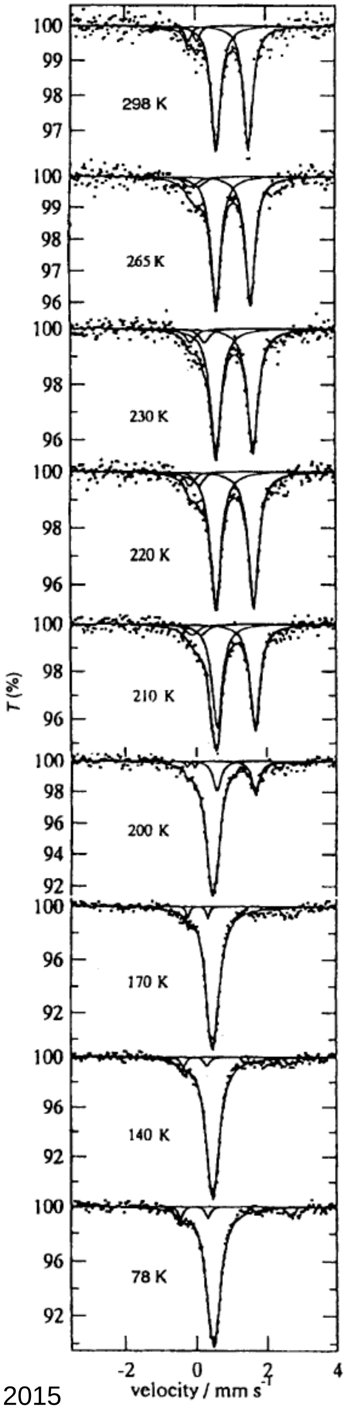




2D layer consisted by Fe and Ni bridged by CN

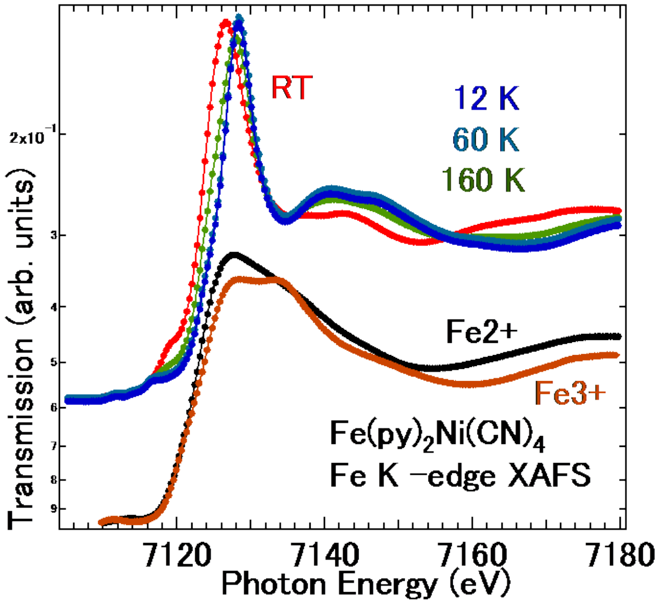
Spin-crossover phenomena

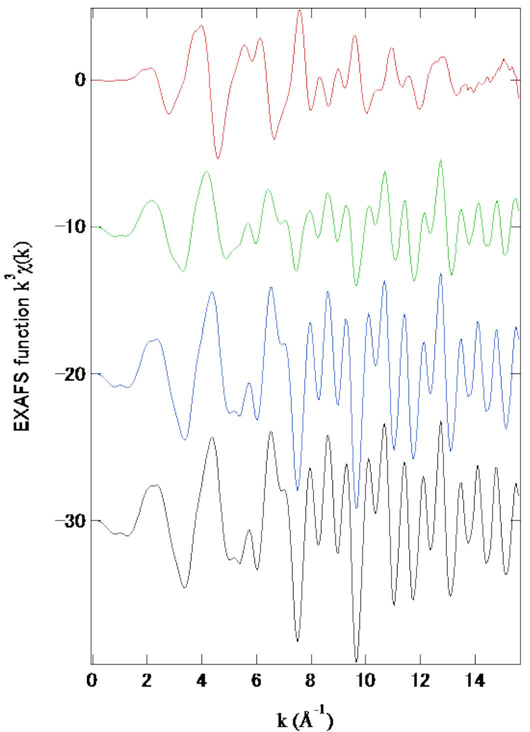


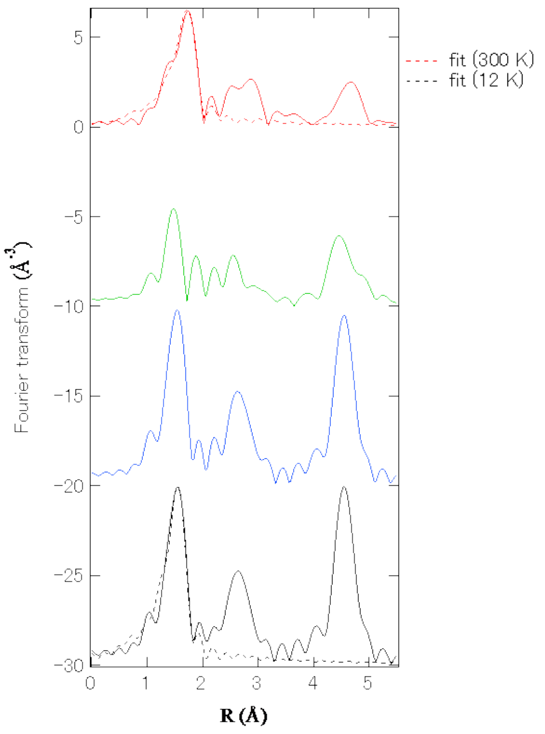


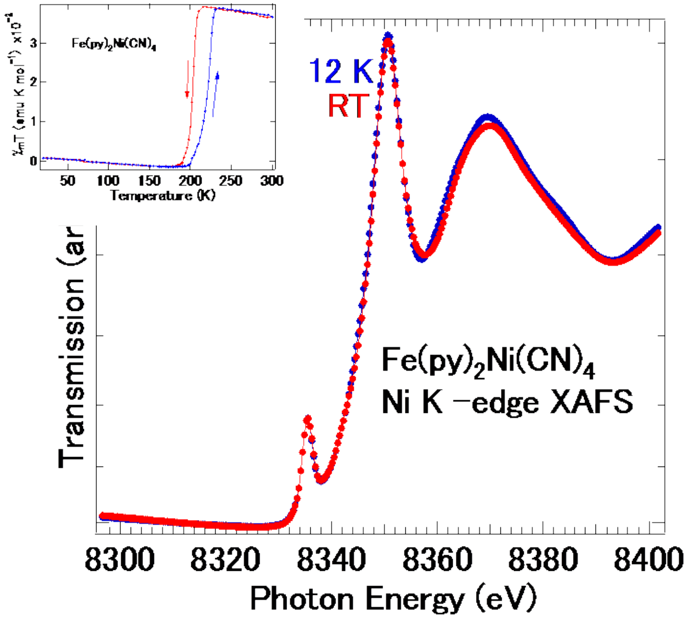
J. Okabayashi et al, 2015

EXAFS of $Fe(py)_2Ni(CN)_4$ complex









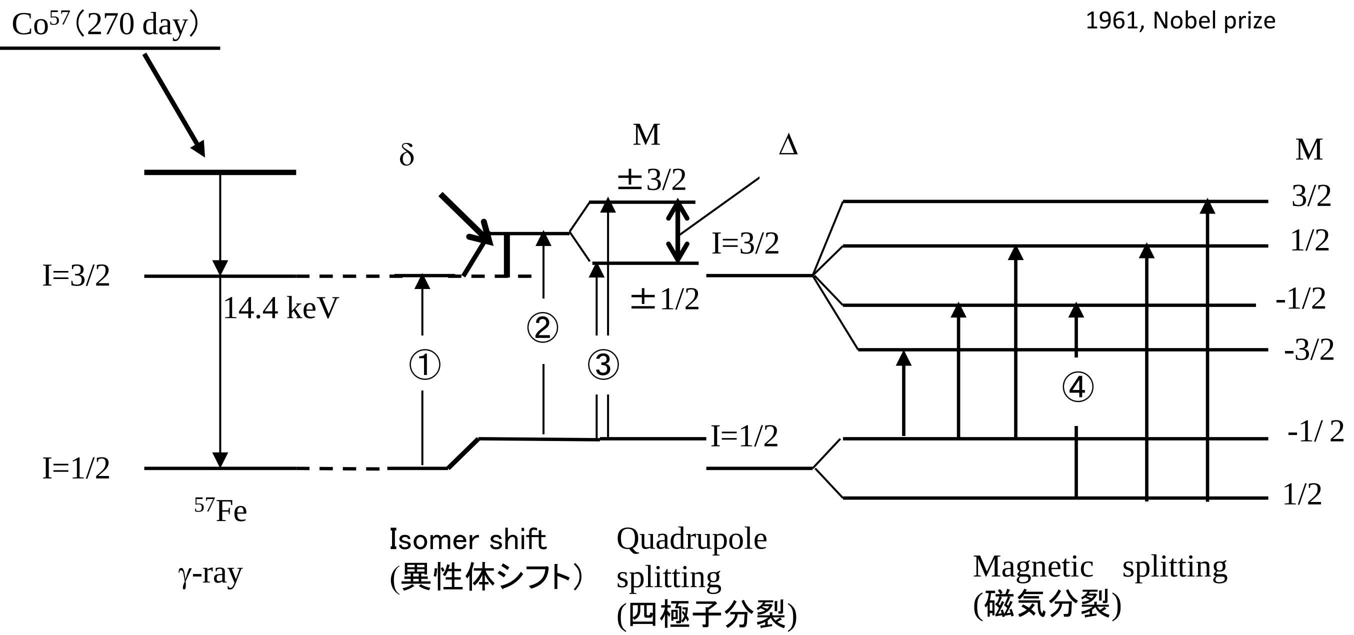
Temp.	HS population	R (Å)	LS population	R (Å)
300 K	1	2.161	-	-
160 K	0.41	2.15	0.59	1.941
60 K	-	-	1	1.940
12 K	-	-	1	1.942

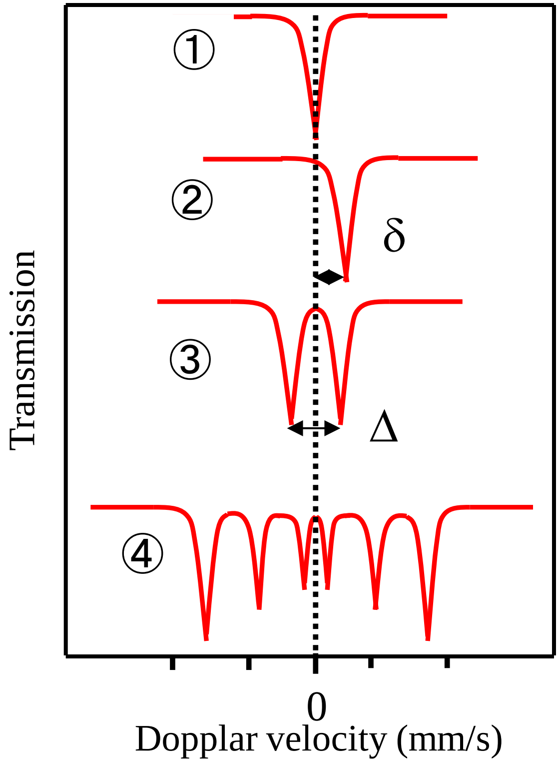
・Fe K-edge XAFS spectra can be explained by the summation of HS and LS states.

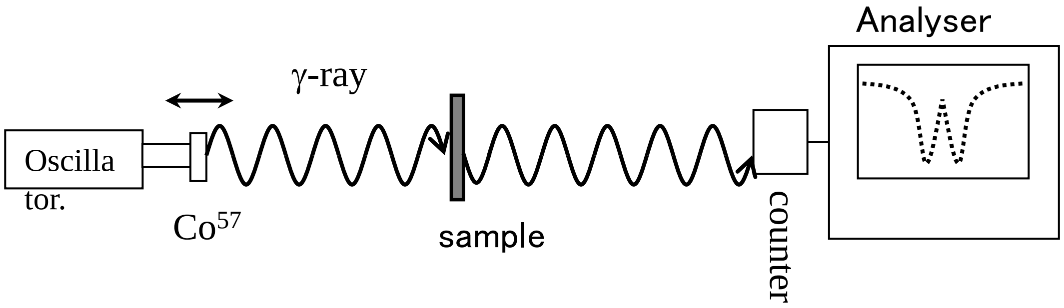
・Bonding distance between Fe-py and Fe-CN becomes equal, which is comparable to that obtained by XRD.

Mössbauer Spectrometry

1961, Nobel prize







Mössbauer Spectroscopy: Local electronic and magnetic structures around Fe

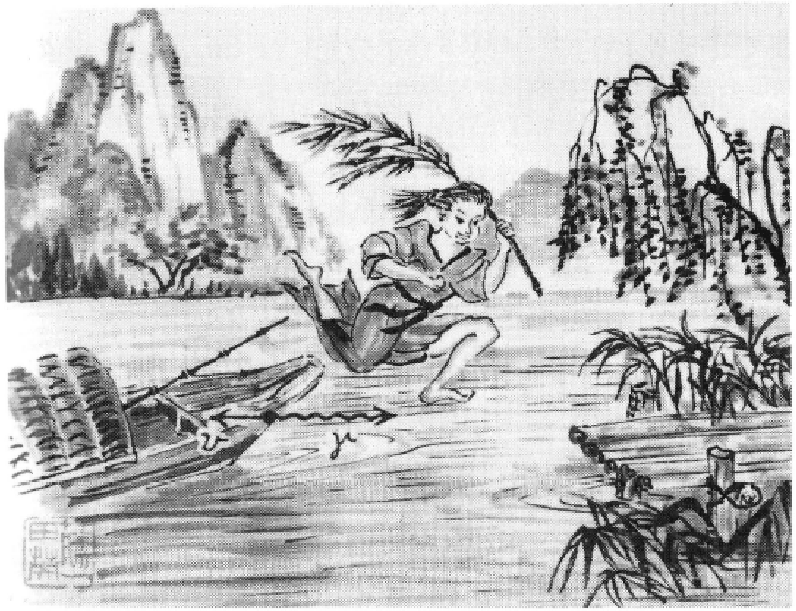
② Isomer shift (IS): Feの価数を反映

③ Quadrupole splitting (QS): Fe周囲の電場勾配を反映

④ Sextet peak: Feの磁気秩序を反映

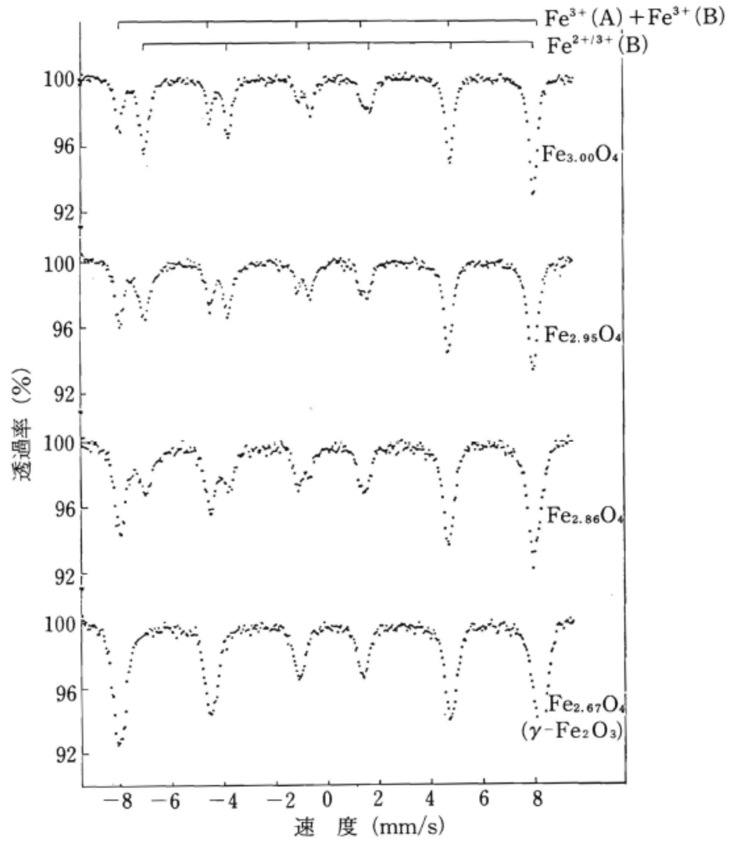
Mössbauer Spectrometry

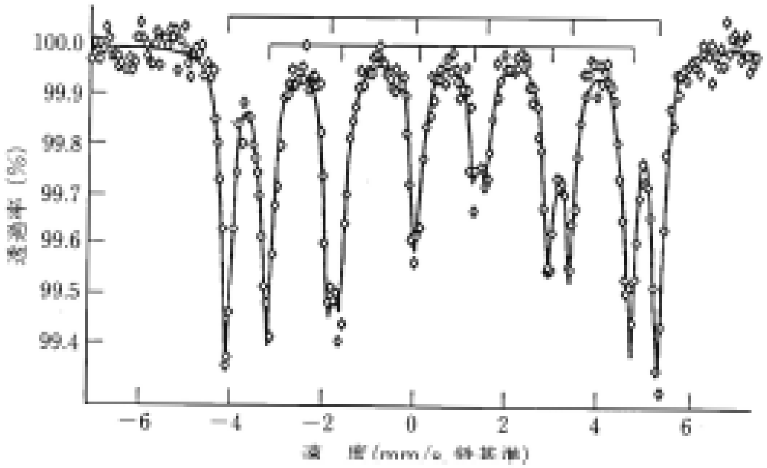
Image for “recoil” effect



藤田英一　メスバウアー分光入門（アグネ社）

Mössbauer Spectrometry

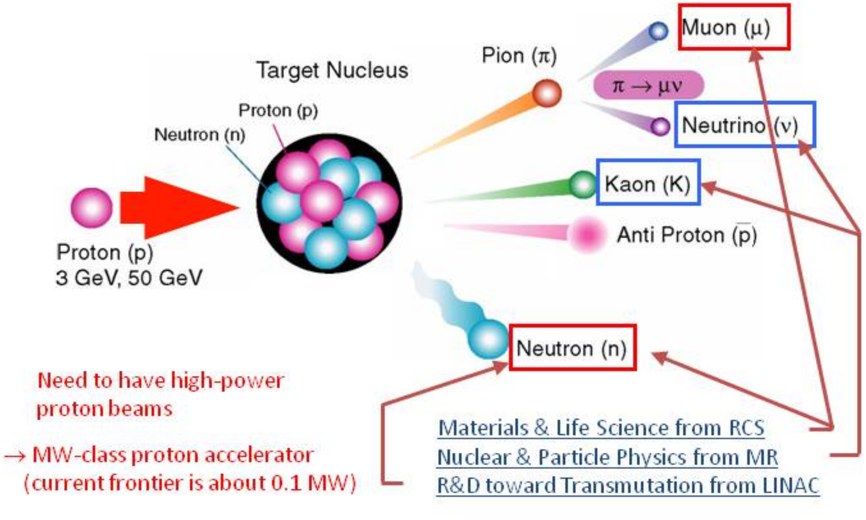




Q19: Explain the principle of Mossbauer spectrometry.

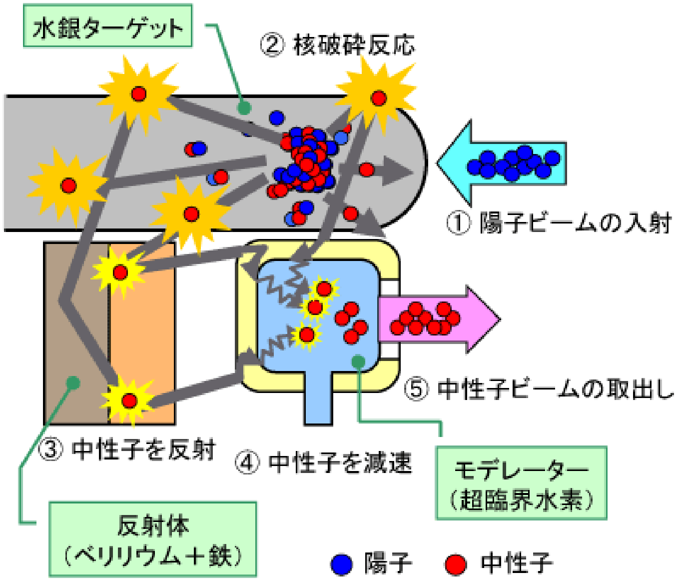
日本分光学会 測定法シリーズ31 メスバウアー分光学 佐野

J-PARC (Japan Proton Accelerator Research Complex) @Tokai



Need to have high-power proton beams
→ MW-class proton accelerator
(current frontier is about 0.1 MW)

Materials & Life Science from RCS
Nuclear & Particle Physics from MR
R&D toward Transmutation from LINAC



① 大強度の陽子ビームを水銀ターゲットに照射する。
② 陽子が水銀の原子核と衝突し、そのとき、原子核を構成していた中性子が高速で飛び出す。
③ 飛び散る中性子を反射体で反射し、モデレーターに集める。
④ 中性子はモデレーター内の水素と衝突を繰り返し、しだいに速度が下がっていく。
⑤ 研究に最適な"速度の遅い"中性子となり、実験装置に導き出される。

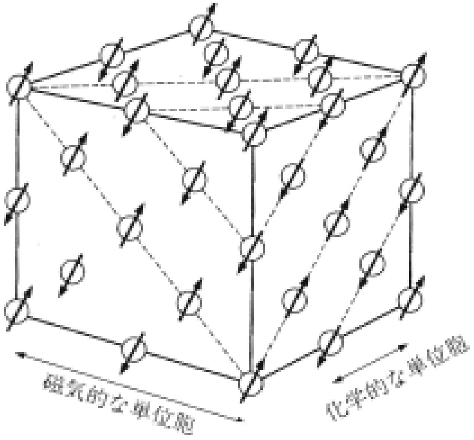
Web page of J-PARC

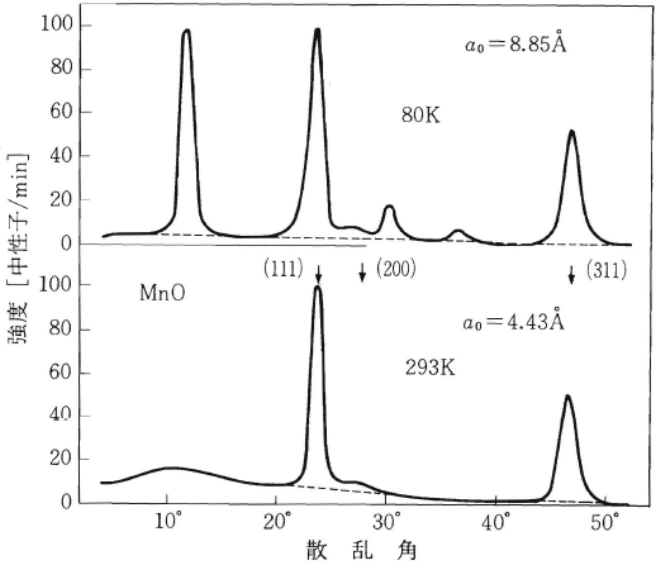
Neutron diffraction

Powerful technique to investigate magnetic structure and crystal structure of hydrogen.

MnO: Antiferromagnetic

$a = 4.43\,\text{Å}$ NaCl-type structure, T_N = 122 K





$\lambda = 1.06\,\text{Å}$ Neutron

$$F(hkl) = b[1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(l+h)}]$$

$$n\lambda = 2d \sin\theta \qquad d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

Q18: Prove *F(hkl)* for fcc-type crystal.

References:

配位子場理論

- 物質の対称性と群論　今野　共立出版
- 金属錯体の現代物性化学　山下、小島　三共出版
- Symmetry and Spectroscopy, Daniel C. Harris, Dover $19.95

- 内殻分光　太田　アイピーシー
-

$$\left\{-\frac{\hbar^2}{2m}\sum_i \Delta_i-\sum_i\sum_{\boldsymbol{R}}\frac{Ze^2}{|\boldsymbol{r}_i-\boldsymbol{R}|}+\sum_{i>j}\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}\right\}\Psi(q_1,\,q_2,\,\cdots,\,q_N)=E\Psi(q_1,\,q_2,\,\cdots,\,q_N)$$

$$\begin{aligned}&-\frac{\hbar^2}{2m}\Delta\psi_\alpha(\boldsymbol{r})+V_{\mathrm{p}}(\boldsymbol{r})\psi_\alpha(\boldsymbol{r})+\sum_\beta\int\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_\beta{}^*(\boldsymbol{r}')\psi_\beta(\boldsymbol{r}')d\boldsymbol{r}'\,\psi_\alpha(\boldsymbol{r})\\&-\sum_\beta\int\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_\beta{}^*(\boldsymbol{r}')\psi_\alpha(\boldsymbol{r}')\psi_\beta(\boldsymbol{r})d\boldsymbol{r}'\\&=E_\alpha\psi_\alpha(\boldsymbol{r})\end{aligned}$$

$$\psi_i(\boldsymbol{r})=\frac{1}{\sqrt{V}}e^{i\boldsymbol{k}_i\cdot\boldsymbol{r}}\times \text{スピン関数}$$

$$\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}=\frac{4\pi e^2}{V}\sum_{\boldsymbol{q}}\frac{1}{q^2}e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}=4\pi e^2\int\frac{d\boldsymbol{q}}{(2\pi)^3}\frac{1}{q^2}e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}$$

$$\begin{aligned}\frac{\hbar^2k^2}{2m}-\frac{1}{V}\sum_{k'<k_{\mathrm{F}}}\frac{4\pi e^2}{|\boldsymbol{k}-\boldsymbol{k}'|^2}&=\frac{\hbar^2k^2}{2m}-\int_{k'<k_{\mathrm{F}}}\frac{d\boldsymbol{k}'}{(2\pi)^3}\frac{4\pi e^2}{|\boldsymbol{k}-\boldsymbol{k}'|^2}\\&=\frac{\hbar^2k^2}{2m}-\frac{2e^2}{\pi}k_{\mathrm{F}}F\left(\frac{k}{k_{\mathrm{F}}}\right)\end{aligned}$$

$$E=2\sum_{k<k_{\mathrm{F}}}\frac{\hbar^2k^2}{2m}-\frac{e^2k_{\mathrm{F}}}{\pi}\sum_{k<k_{\mathrm{F}}}\left[1+\frac{k_{\mathrm{F}}{}^2-k^2}{2kk_{\mathrm{F}}}\ln\left|\frac{k_{\mathrm{F}}+k}{k_{\mathrm{F}}-k}\right|\right]$$

$$E=N\left(\frac{3}{5}E_{\mathrm{F}}-\frac{3}{4}\frac{e^2}{\pi}k_{\mathrm{F}}\right)$$

$$\frac{E}{N}=\frac{e^2}{2a_0}\left[\frac{3}{5}(k_{\mathrm{F}}a_0)^2-\frac{3}{2\pi}(k_{\mathrm{F}}a_0)\right]=\left[\frac{2.21}{(r_{\mathrm{s}}/a_0)^2}-\frac{0.916}{(r_{\mathrm{s}}/a_0)}\right]\mathrm{Ry}$$

$$\frac{E}{N}=\left[\frac{2.21}{(r_{\mathrm{s}}/a_0)^2}-\frac{0.916}{(r_{\mathrm{s}}/a_0)}+0.0622\ln(r_{\mathrm{s}}/a_0)-0.096+O(r_{\mathrm{s}}/a_0)\right]$$

相関エネルギー(correlation energy)

1個の伝導電子が占める体積を球でおきかえたときの半径 r_{s}

$$V/N=4\pi r_{\mathrm{s}}^3/3$$

電子の運動エネルギーは $r_{\mathrm{s}}{}^{-2}$ に比例

クーロン相互作用は $r_{\mathrm{s}}{}^{-1}$ に比例

電子密度を小さくして r_{s} を大きく

あるところでクーロンエネルギーが運動エネルギーより大きく

低密度の極限では電子はなるべく離れた位置に

クーロンエネルギーを下げようとする

電子の結晶化であり、**ウィグナー結晶**とよば

$$\delta u(\boldsymbol{r},\, t) = u e^{i\boldsymbol{q}\cdot\boldsymbol{r}} e^{i\omega t + \alpha t}$$

$$\phi_{\boldsymbol{k}} = \frac{1}{\sqrt{V}} \exp\left\{ i\left(\boldsymbol{k}\cdot\boldsymbol{r} + \frac{E_{\boldsymbol{k}}}{\hbar} t \right) \right\}$$

$$\psi_{\boldsymbol{k}} = \phi_{\boldsymbol{k}} + C_{\boldsymbol{k}+\boldsymbol{q}}(t) \phi_{\boldsymbol{k}+\boldsymbol{q}}$$

$$C_{\boldsymbol{k}+\boldsymbol{q}}(t) = \frac{u e^{i\omega t + \alpha t}}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} + \hbar\omega - i\hbar\alpha}$$

$$\begin{aligned} \delta\rho(\boldsymbol{r},\, t) &= e \sum_{\boldsymbol{k}} \{ |\psi_{\boldsymbol{k}}(\boldsymbol{r},\, t)|^2 - 1 \} \\ &\simeq \frac{e}{V} \sum_{\boldsymbol{k}} C_{\boldsymbol{k}+\boldsymbol{q}}(t) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} + C_{\boldsymbol{k}+\boldsymbol{q}}{}^*(t) e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \end{aligned}$$

$$\delta\rho = \frac{e}{V} \sum_{\boldsymbol{k}} f(\boldsymbol{k}) \left\{ \frac{u}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} + \hbar\omega - i\hbar\alpha} + \frac{u}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}-\boldsymbol{q}} - \hbar\omega + i\hbar\alpha} \right\} e^{i\boldsymbol{q}\cdot\boldsymbol{r} + i\omega t + \alpha t} + \text{c.c.}$$

$$\boldsymbol{k} - \boldsymbol{q} \rightarrow \boldsymbol{k} \qquad \delta\rho = \frac{eu}{V} \sum_{\boldsymbol{k}} \left\{ \frac{f(\boldsymbol{k}) - f(\boldsymbol{k}+\boldsymbol{q})}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} + \hbar\omega - i\hbar\alpha} \right\} e^{i\boldsymbol{q}\cdot\boldsymbol{r} + i\omega t + \alpha t} + \text{c.c.}$$

$$\Delta(\delta\Phi) = -4\pi e \delta\rho \qquad \delta\Phi(\boldsymbol{r},\, t) = \Phi e^{i\boldsymbol{q}\cdot\boldsymbol{r} + i\omega t + \alpha t} + \text{c.c.}$$

$$\Phi = \frac{4\pi e^2}{q^2 V} \sum_{\boldsymbol{k}} \frac{f(\boldsymbol{k}) - f(\boldsymbol{k}+\boldsymbol{q})}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} + \hbar\omega - i\hbar\alpha} u$$

$$\delta V(\boldsymbol{r},\, t) = V e^{i\boldsymbol{q}\cdot\boldsymbol{r} + i\omega t + \alpha t} + \text{c.c.}$$

$$\delta u(\boldsymbol{r},\, t) = \delta V(\boldsymbol{r},\, t) + \delta\Phi(\boldsymbol{r},\, t)$$

$$u = V - \frac{4\pi e^2}{q^2 V} \sum_{\boldsymbol{k}} \frac{f(\boldsymbol{k}) - f(\boldsymbol{k}+\boldsymbol{q})}{E_{\boldsymbol{k}+\boldsymbol{q}} - E_{\boldsymbol{k}} - \hbar\omega + i\hbar\alpha} u$$

$$\varepsilon(\boldsymbol{q},\, \omega) = 1 + \frac{4\pi e^2}{q^2 V} \sum_{\boldsymbol{k}} \frac{f(\boldsymbol{k}) - f(\boldsymbol{k}+\boldsymbol{q})}{E_{\boldsymbol{k}+\boldsymbol{q}} - E_{\boldsymbol{k}} - \hbar\omega + i\hbar\alpha}$$

$$u = \frac{V}{\varepsilon(\boldsymbol{q}, \omega)}$$

$$\delta V(\boldsymbol{r}, t) = \iint V(\boldsymbol{q}, \omega) e^{i\boldsymbol{q}\cdot\boldsymbol{r}+i\omega t} d\boldsymbol{q} d\omega$$

$$\delta u(\boldsymbol{r}, t) = \iint \frac{V(\boldsymbol{q}, \omega)}{\varepsilon(\boldsymbol{q}, \omega)} e^{i\boldsymbol{q}\cdot\boldsymbol{r}+i\omega t} d\boldsymbol{q} d\omega$$

$\omega=0,\ \boldsymbol{q}\simeq 0$

$$E_{\boldsymbol{k}+\boldsymbol{q}} - E_{\boldsymbol{k}} \simeq \boldsymbol{q}\cdot\nabla_{\boldsymbol{k}} E_{\boldsymbol{k}}$$

$$f(\boldsymbol{k}) - f(\boldsymbol{k}+\boldsymbol{q}) \simeq -\boldsymbol{q}\cdot\frac{\partial f}{\partial E_{\boldsymbol{k}}}\nabla_{\boldsymbol{k}} E_{\boldsymbol{k}}$$

$$\varepsilon(\boldsymbol{q}, 0) = 1 + \frac{4\pi e^2}{q^2 V}\int\left(-\frac{\partial f}{\partial E}\right) D(E) dE = 1 + \frac{\lambda^2}{q^2}$$

$$\lambda^2 = 4\pi e^2 D(E_{\mathrm{F}})/V$$

$$\int d\boldsymbol{q} \frac{4\pi e^2}{q^2 V} \frac{q^2}{q^2+\lambda^2} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} = \frac{e^2}{r} e^{-\lambda r}$$

$E_{\boldsymbol{k}+\boldsymbol{q}} - E_{\boldsymbol{k}} \ll \hbar\omega$

$$\varepsilon(\boldsymbol{q}, \omega) = 1 + \frac{4\pi e^2}{q^2 V}\sum_{\boldsymbol{k}} \frac{2f(\boldsymbol{k})(E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}})}{(\hbar\omega)^2 - (E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}})^2}$$

$$\varepsilon(\boldsymbol{q}, \omega) = 1 + \frac{4\pi e^2}{q^2 V}\sum_{\boldsymbol{k}} \frac{f(\boldsymbol{k})}{(\hbar\omega)^2}\left(-q^2\frac{\partial^2 E}{\partial k^2}\right) = 1 - \frac{4\pi n e^2}{\omega^2 m}$$

$$\omega_{\mathrm{P}} = \sqrt{\frac{4\pi n e^2}{m}}$$

$$\varepsilon(\boldsymbol{q}, \omega) = 1 - \frac{{\omega_{\mathrm{P}}}^2}{\omega^2}$$