



2022.5.11 Lecture 5

10:25 – 11:55

Lecture on

# Magnetic Properties of Materials

## 磁性 (Magnetism)

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# Review of last four lectures

## Chapter 1 Basic Notions of Magnetism

Classical pictures of magnetic moments in materials:

- Magnetic charges
- Circular currents

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

Quest for the sources of magnetic dipoles in materials.

Spins and spin-orbit interactions

## Chapter 2 Magnetism of Localized Electrons

Spherical potential, closed shell magnetization

Electronic states of magnetic ions

- LS (j-j) coupling, Hund's rule
- Ligand field

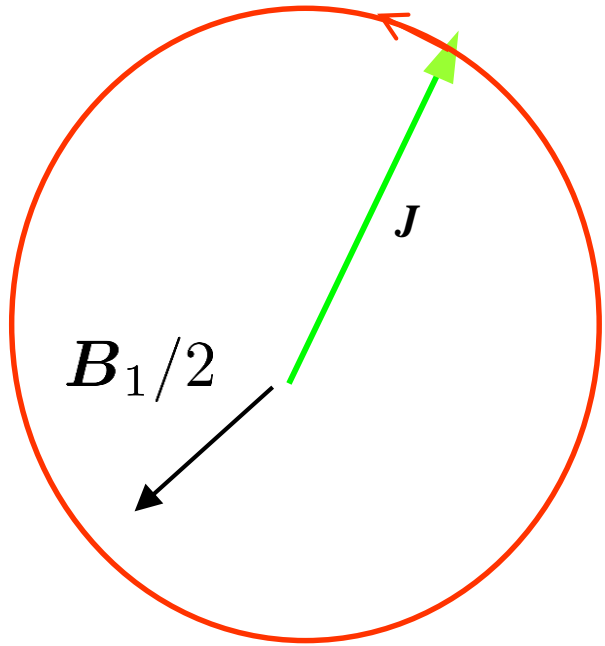
Representative experimental method: magnetic resonance

- Magnetic resonance (continued)
- Spin Hamiltonian
- Example of analyzing experimental data on electron paramagnetic resonance
- Application of paramagnetism: magnetic refrigeration

## Chapter 3 Magnetism of conduction electrons

- Pauli paramagnetism
- Landau diamagnetism

# Magnetic resonance (2)



High frequency magnetic field in  $xy$ -plane

$$\begin{aligned} \mathbf{B}(t) &= \mathbf{B}_1 \cos(\omega t) \\ &= \frac{\mathbf{B}_1}{2} [\exp(i\omega t) + \exp(-i\omega t)] \end{aligned} \quad \text{Two rotational magnetic fields}$$

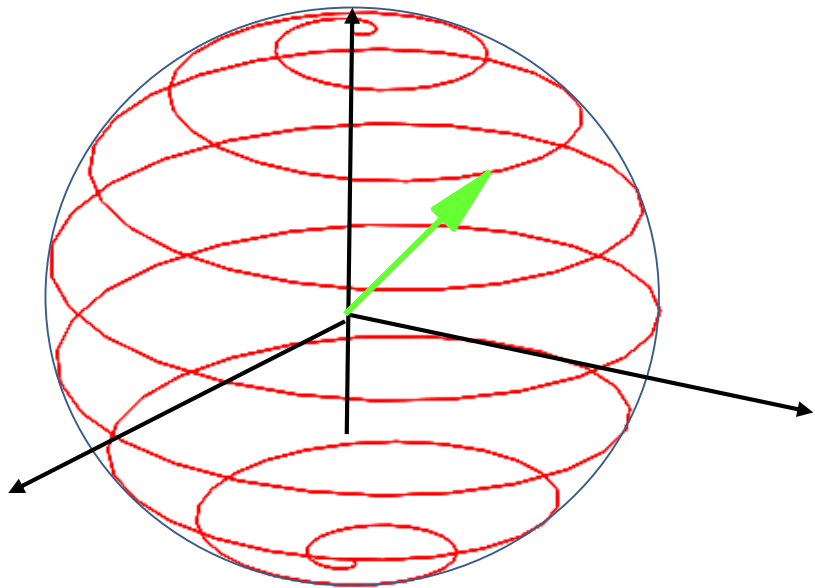
when  $\omega \approx \omega_L$

On the rotational coordinate:  $\omega \approx 0, 2\omega_L$

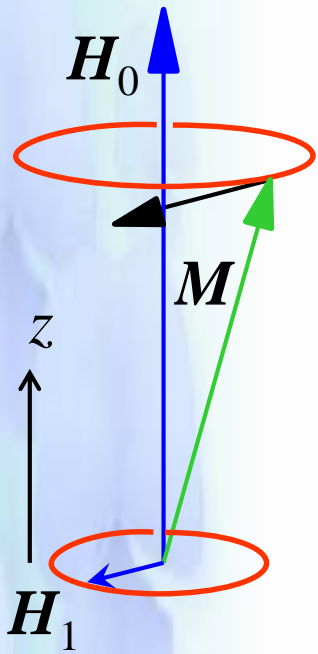
Ignore  $2\omega_L$  component: rotational wave approximation

$$\text{Precession around } \mathbf{B}_1 \quad \omega_1 = g_j \frac{eB_1}{2m}$$

Total motion: spiral



# Magnetic resonance



Macroscopic magnetization  $\mathbf{M}$

Classical equation of motion

Phenomenological introduction of relaxation time

$T_1$ : energy relaxation time,  $T_2$ : phase relaxation time

$\mathbf{H}_0$ : static field (z)

$\mathbf{H}_1$ : rotating field with  $-\omega$

$$\left\{ \begin{array}{l} \frac{dM_z}{dt} = \gamma[\mathbf{M} \times \mathbf{H}]_z + \frac{M_0 - M_z}{T_1}, \\ \frac{dM_{x,y}}{dt} = \gamma[\mathbf{M} \times \mathbf{H}]_{x,y} - \frac{M_{x,y}}{T_2}. \end{array} \right.$$

$$\left. \begin{array}{l} \mathbf{H}_0: \text{static field (z)} \\ \mathbf{H}_1: \text{rotating field with } -\omega \end{array} \right\} \mathbf{H} = \left( \frac{H_1}{2} \cos \omega t, -\frac{H_1}{2} \sin \omega t, H_0 \right)$$

Then the equation of motion is given as

$$\left\{ \begin{array}{l} \frac{dM_x}{dt} = \gamma \left[ M_y H_0 + M_z \frac{H_1}{2} \sin \omega t \right] - \frac{M_x}{T_2}, \\ \frac{dM_y}{dt} = \gamma \left[ M_z \frac{H_1}{2} \cos \omega t - M_x H_0 \right] - \frac{M_y}{T_2}, \\ \frac{dM_z}{dt} = \gamma \left[ -M_x H_1 \sin \omega t - M_y \frac{H_1}{2} \cos \omega t \right] + \frac{M_0 - M_z}{T_1} \end{array} \right.$$

# Magnetic resonance (2)

We introduce the coordinate system  $(x', y', z')$  rotating around  $z$ -axis with freq.  $\omega$ .

$$\begin{cases} M_{x'} = M_x \cos \omega t - M_y \sin \omega t, \\ M_{y'} = M_x \sin \omega t + M_y \cos \omega t \end{cases}$$

conditions

$$\begin{cases} \frac{dM_{x'}}{dt} = \frac{dM_{y'}}{dt} = 0 & \text{(stationary state),} \\ M_z \simeq M_0 = \chi_0 H_0 & \text{(oblique angle is small)} \end{cases}$$

Solution

$$\begin{cases} M_{x'} = \chi_0 \omega_0 T_2 \frac{(\omega_0 - \omega) T_2 H_1 / 2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 (H_1 / 2)^2 T_1 T_2} \\ M_{y'} = \chi_0 \omega_0 T_2 \frac{H_1 / 2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 (H_1 / 2)^2 T_1 T_2} \end{cases}$$

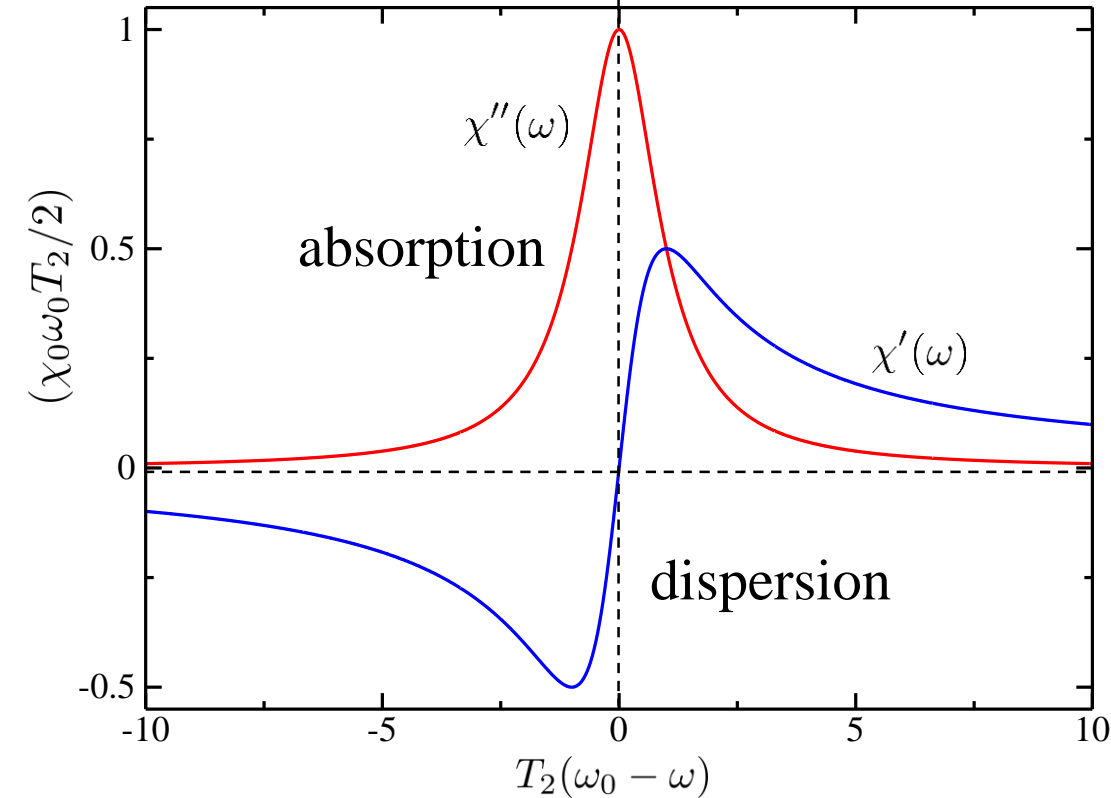
Original coordinate

$$\begin{aligned} M_x &= \chi'(\omega) H_1 \cos \omega t + \chi''(\omega) H_1 \sin \omega t, \\ M_y &= -\chi'(\omega) H_1 \sin \omega t + \chi''(\omega) H_1 \cos \omega t \end{aligned}$$

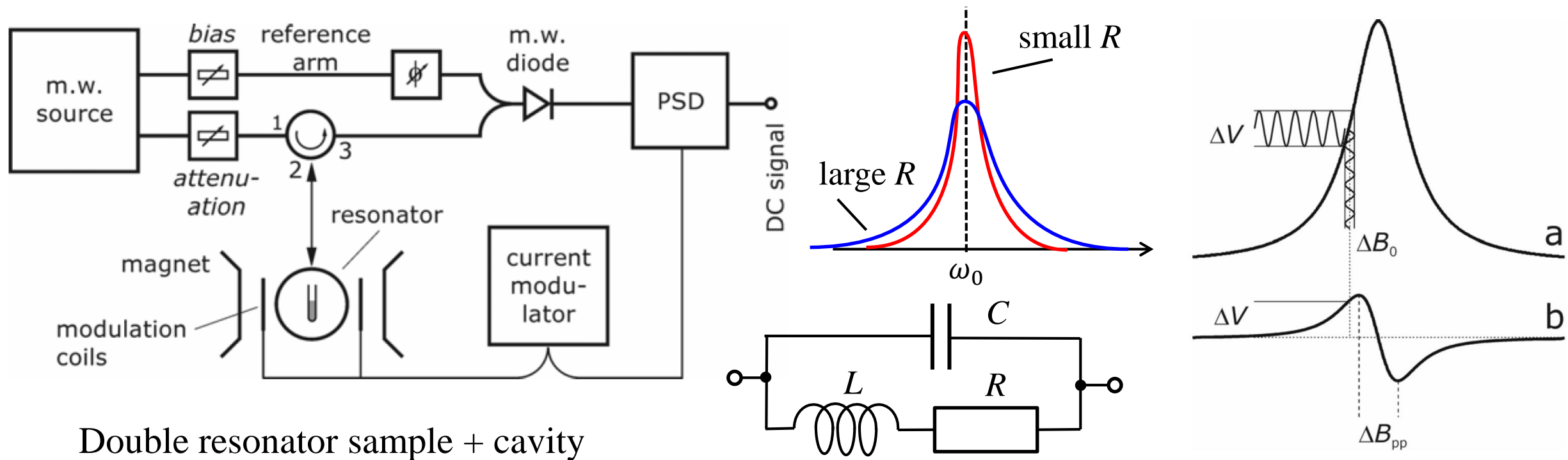
large relaxation

$$\gamma^2 H_1^2 T_1 T_2 \ll 1$$

$$\begin{aligned} \chi'(\omega) &= \frac{\chi_0 \omega_0}{2} T_2 \frac{(\omega_0 - \omega) T_2}{1 + (\omega_0 - \omega)^2 T_2^2}, \\ \chi''(\omega) &= \frac{\chi_0 \omega_0}{2} T_2 \frac{1}{1 + (\omega_0 - \omega)^2 T_2^2} \end{aligned}$$



# Electron paramagnetic resonance (EPR) experimental setup



Double resonator sample + cavity

Continuous wave (CW) measurement: detection of resonance dissipation

Pulse, Fourier transform measurement: detection of magnetic field due to the precession of magnetic moment

# Spin Hamiltonian

For the comparison of the theory with EPR experiments we need to go a little further in approximation.

Effective spin Hamiltonian: Only contains spin operators, i.e. the orbital part is already  
(in case  $\mathcal{H}_{\text{CF}}$  is diagonalized) integrated out.

---

{o} Orbital basis:  $\{\varphi_0, \varphi_1, \dots, \}$  diagonalizes  $\mathcal{H}_{\text{orb}} = \mathcal{H}_0 + \mathcal{H}_{\text{CF}}$   
In ket form:  $|\varphi_n\rangle = |n\rangle_{\text{o}}$   
Energy eigenstates:  ${}_{\text{o}}\langle n | \mathcal{H}_{\text{orb}} | n' \rangle_{\text{o}} = E_n \delta_{nn'}$

---

{s} Spin basis for total spin  $S$ :  $\{\phi_{-2S}, \phi_{-2S+1}, \dots, \phi_{2S}\}$   
In ket form:  $|\phi_m\rangle = |m\rangle_{\text{s}}$

---

Perturbation Hamiltonian:  $\mathcal{H}' = \lambda \mathbf{L} \cdot \mathbf{S} + \mu_{\text{B}} (\mathbf{L} + g_e \mathbf{S}) \cdot \mathbf{H}$   $g_e$  : g-factor of electron  
spin-orbit Zeeman

Expand the wavefunction with {o} and {s} as:

$$\Psi = \sum_{nm} a_{nm} \varphi_n \phi_m = \sum_{nm} a_{nm} |n\rangle_{\text{o}} |m\rangle_{\text{s}}$$



# Spin Hamiltonian (2)

Eigenenergy equation:

$$\mathcal{H}\Psi = (\mathcal{H}_{\text{orb}} + \mathcal{H}')\Psi = E\Psi.$$

Second order perturbation in energy:

$$\tilde{\mathcal{H}} = {}_o\langle 0|\mathcal{H}'|0\rangle_o + \sum_{n \neq 0} \frac{{}_o\langle 0|\mathcal{H}'|n\rangle_o {}_o\langle n|\mathcal{H}'|0\rangle_o}{E_0 - E_n}$$

Orbital angular momentum is quenched:

$${}_o\langle 0|\mathbf{L}|0\rangle_o = 0 \longrightarrow {}_o\langle 0|\mathcal{H}'|0\rangle_o = g_e\mu_B \mathbf{S} \cdot \mathbf{H}$$

The second order term

→ reduced to second order in  $\mathbf{L}$ :

$${}_o\langle 0|\mathcal{H}'|n\rangle_o = {}_o\langle 0|\mathbf{L}|n\rangle_o \cdot \underline{(\lambda\mathbf{S} + \mu_B\mathbf{H})}$$

effective magnetic field for  $\mathbf{L}$

The effective spin Hamiltonian:

$$\tilde{\mathcal{H}} = g_e\mu_B \mathbf{S} \cdot \mathbf{H} - (\lambda\mathbf{S} + \mu_B\mathbf{H})\Lambda(\lambda\mathbf{S} + \mu_B\mathbf{H})$$

where  $\Lambda$  is a tensor given by

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{{}_o\langle 0|L_i|n\rangle_o {}_o\langle n|L_j|0\rangle_o}{E_n - E_0} \quad (i, j = x, y, z)$$

Expansion:

$$\tilde{\mathcal{H}} = \mu_B \mathbf{S} g_e (\mathbf{1} - \lambda\Lambda)\mathbf{H} - \lambda^2 \mathbf{S}\Lambda\mathbf{S} - \mu_B^2 \mathbf{H}\Lambda\mathbf{H}$$

# Spin Hamiltonian (3)

$$\tilde{\mathcal{H}} = \mu_B \mathbf{S} g_e (\mathbf{1} - \lambda \Lambda) \mathbf{H} - \lambda^2 \mathbf{S} \Lambda \mathbf{S} - \mu_B^2 \mathbf{H} \Lambda \mathbf{H}$$

The third term is small, does not contribute to level splitting → Drop

The first term: extension of Zeeman energy with effective g-tensor:

$$\tilde{\mathbf{g}} = g_e (\mathbf{1} - \lambda \Lambda)$$

The second term is written as

$$-\lambda^2 \mathbf{S} \Lambda \mathbf{S} = D \left[ S_z^2 - \frac{S(S+1)}{3} \right] + E(S_x^2 - S_y^2)$$

principal axes:  $x, y, z$

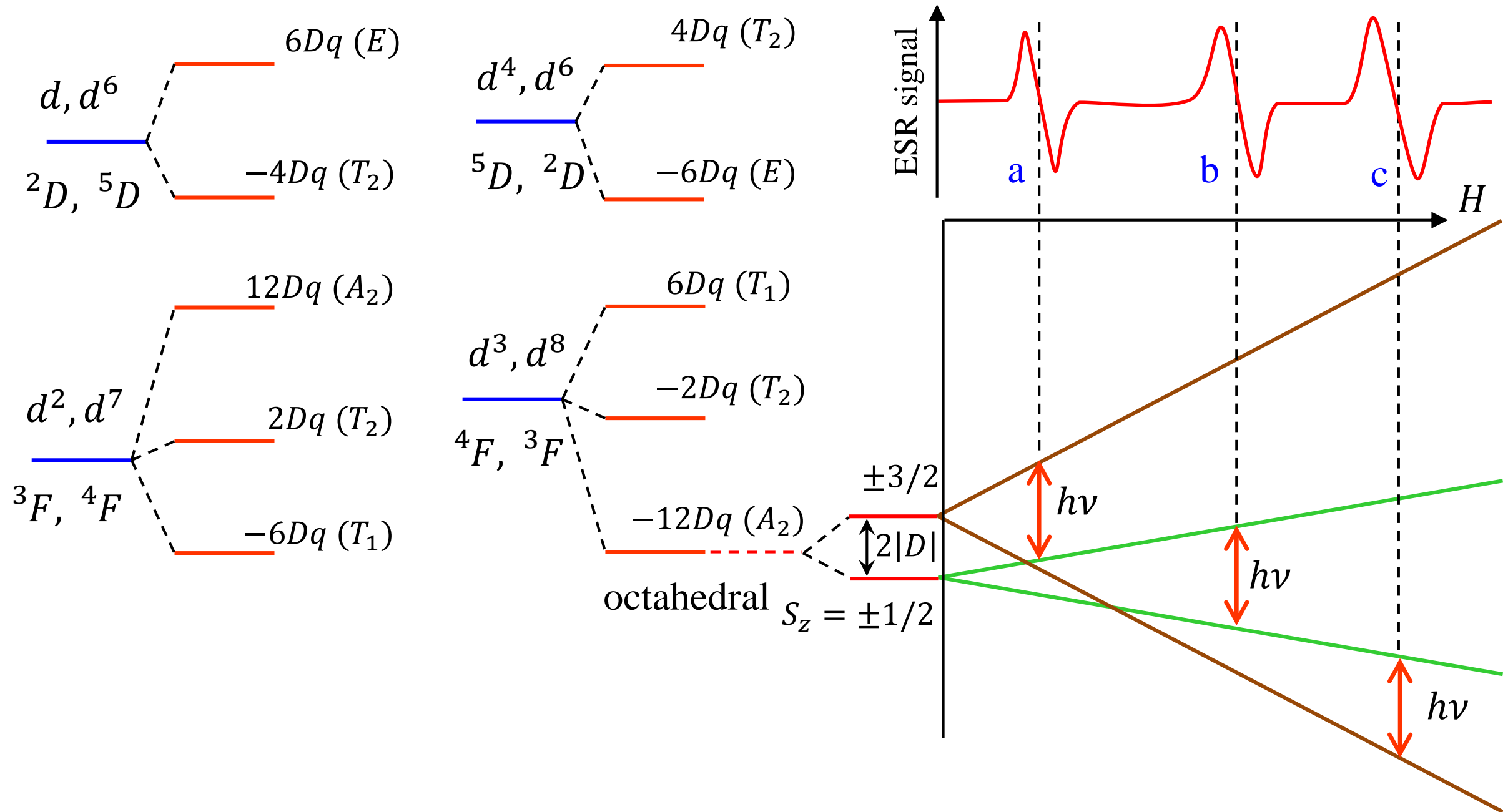
$D$ : axial fine structure parameter

$E$ : rhombic fine structure parameter

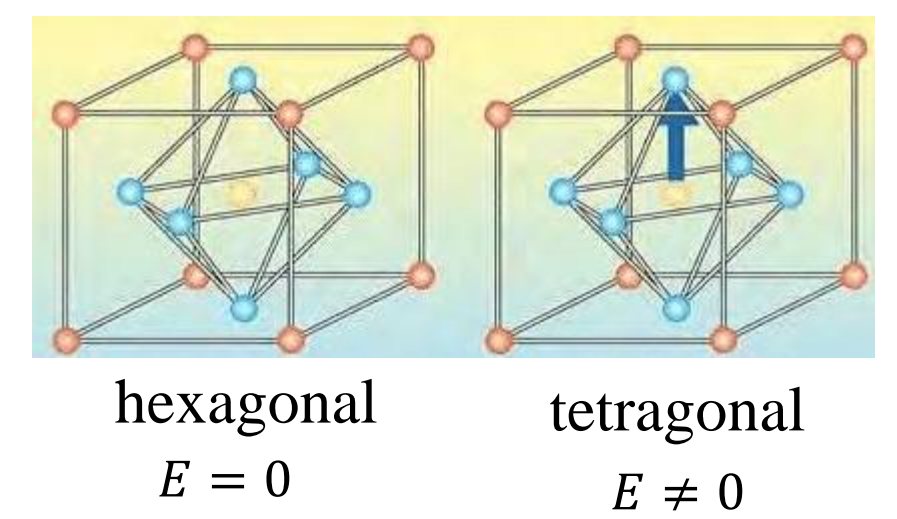
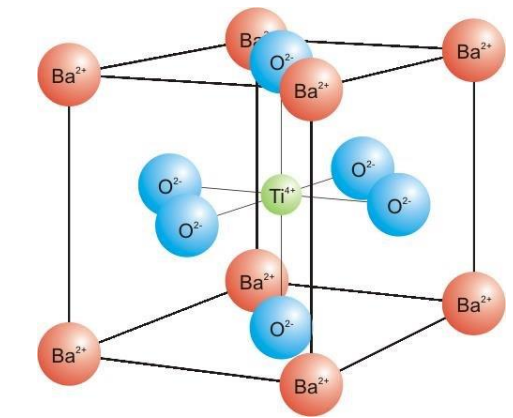
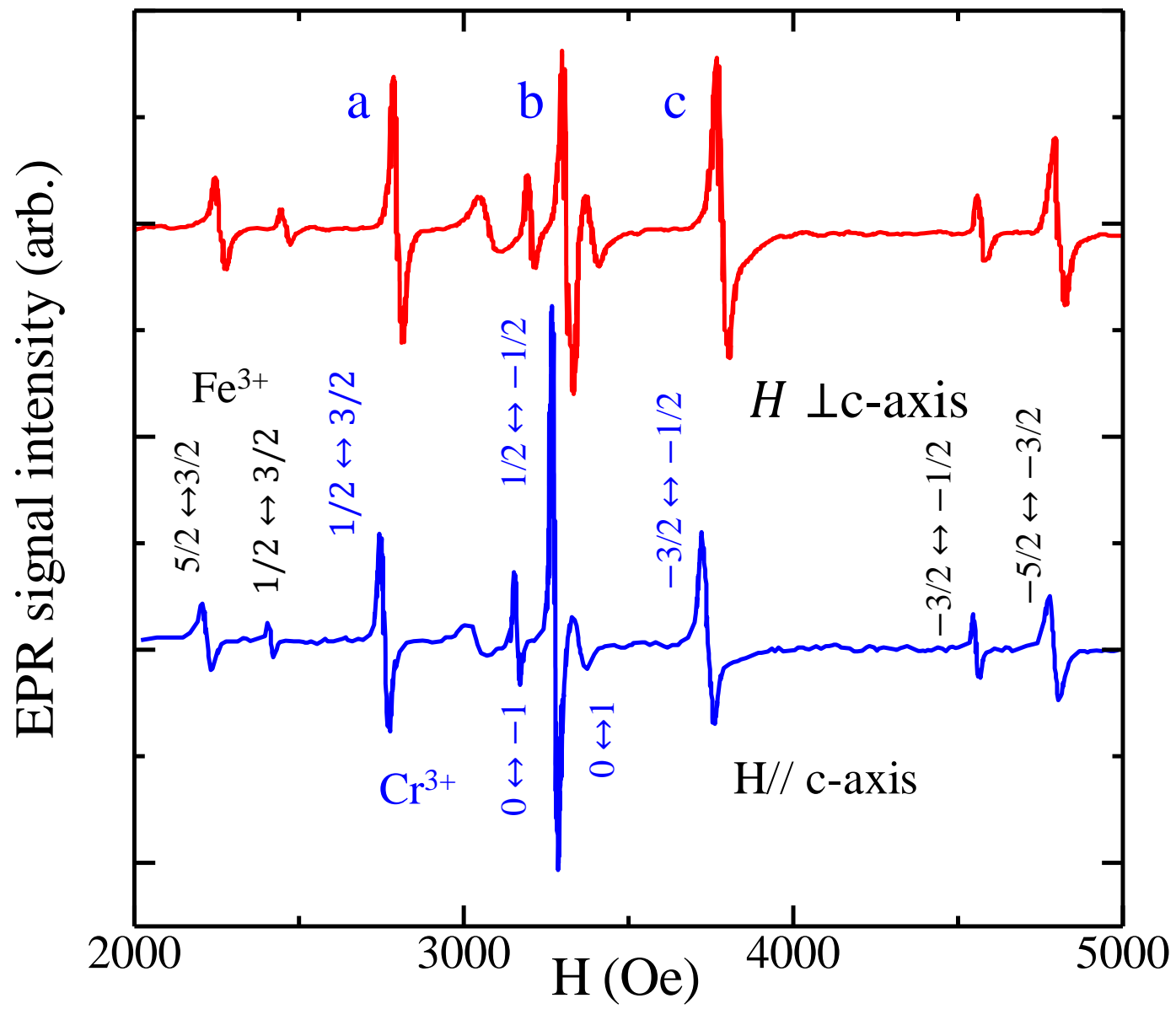
The form frequently used for the analysis of experiments

$$\tilde{\mathcal{H}} = \mu_B \mathbf{S} \tilde{\mathbf{g}} \mathbf{H} + D \left[ S_z^2 - \frac{S(S+1)}{3} \right] + E(S_x^2 - S_y^2)$$

# Weak crystal field approximation



# EPR signal from $\text{Cr}^{3+}$ and $\text{Fe}^{3+}$ ions in $\text{BaTiO}_3$

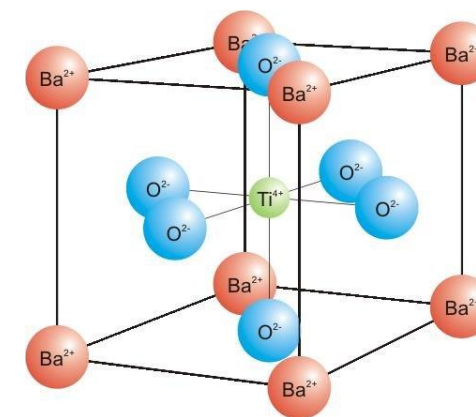


Bairavarasu et al. SPIE Proc. 6698-05

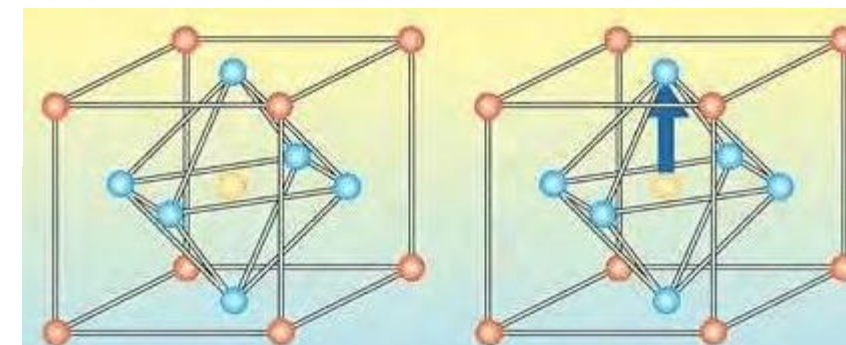
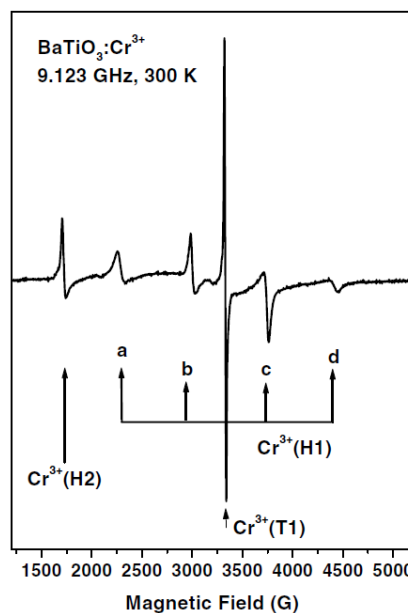
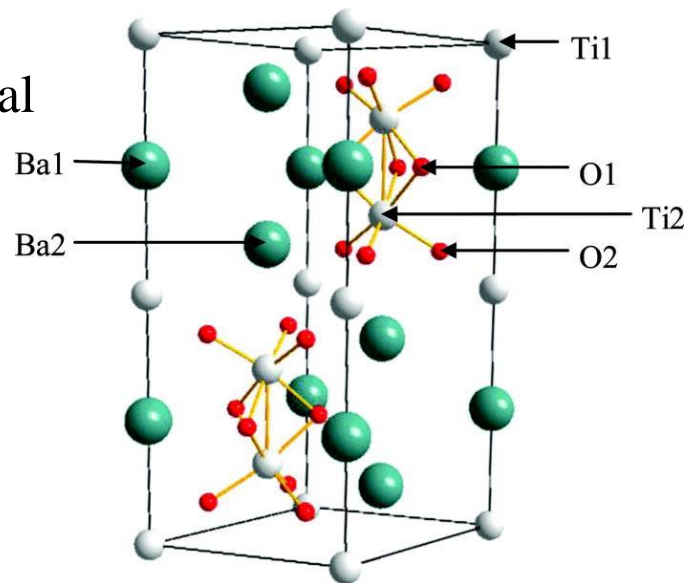


# EPR signal from $\text{Cr}^{3+}$ and $\text{Fe}^{3+}$ ions in $\text{BaTiO}_3$

Ion	Crystal	g	$ D $ ( $\text{cm}^{-1}$ )	$ E $ ( $\text{cm}^{-1}$ )
$\text{Fe}^{3+}$	$\text{BaTiO}_3$	2.000	0.022	0.0079
	another report	2.003	0.0987	
$\text{Cr}^{3+}$	$\text{BaTiO}_3$	1.975	0.046	0.0055
	h- $\text{BaTiO}_3$	H1 $g_z =$	1.9797	0.105
		H1 $g_{x,y} =$	1.9857	
		H2 $g_z =$	1.9736	0.3220
H2 $g_{x,y} =$		1.9756		



hexagonal



cubic  
 $E = 0$

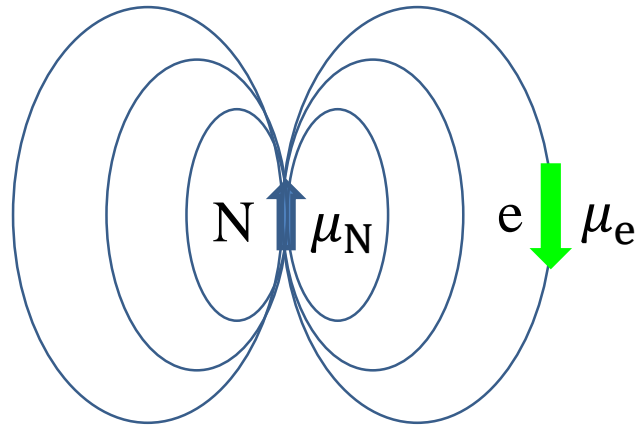
tetragonal  
 $E \neq 0$

Boettcher et al. JPCM **17**, 2763 (2005)

Bairavarasu et al. SPIE Proc. 6698-05

# Hyperfine structures

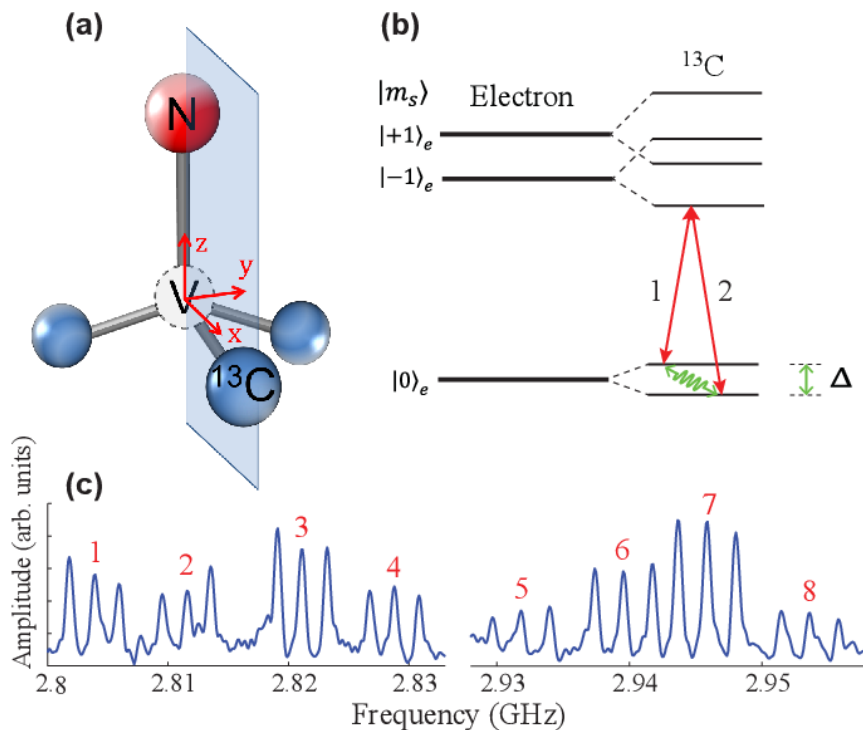
electron-nuclear spin exchange interaction:



$\mathcal{H}_{\text{HF}} = A \mathbf{I} \cdot \mathbf{J}$  the same form as spin-orbit interaction

$$\mathbf{F} = \mathbf{I} + \mathbf{J}$$

$$\begin{aligned} \mathcal{H}_{\text{HF}} |F, M_F\rangle &= A \frac{\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{J}^2}{2} |F, M_F\rangle \\ &= A \frac{F(F+1) - I(I+1) - J(J+1)}{2} |F, M_F\rangle \end{aligned}$$



NV center

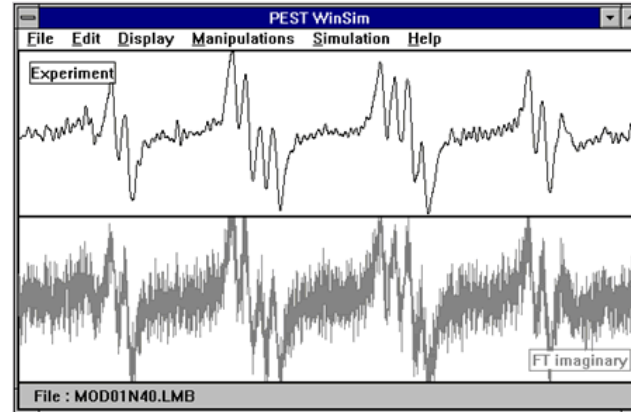
Rama et al., PRB 94, 060101 (2016).

# ESR detector/analyzer

## EPR public software

### EPR-WinSim

<https://www.niehs.nih.gov/research/resources/software/tox-pharm/tools/>



### Easyspin

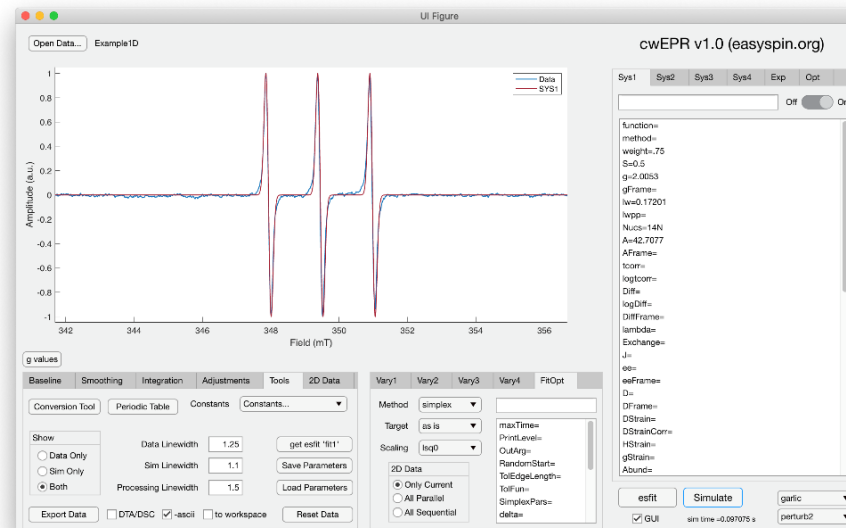
<https://www.easyspin.org/>

## Works on MATLAB

GUI front: cwEPR etc.

## Announcement of Easyspin for Octave

<https://octave.discourse.group/t/easyspin-for-octave/1177>



# Commercial machines

JEOL 日本電子株式会社 ESR装置

製品情報 APPLICATIONS NOTES サービス&ソリューション 会社情報 採用情報

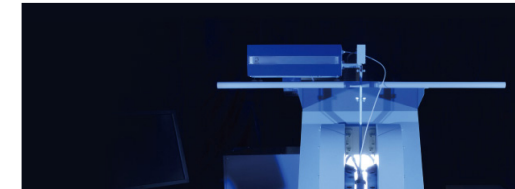
特長 仕様/オプション アプリケーション 関連製品 more info

## 特長

JES-X3シリーズは、低雑音Gunn発振器を改良し従来より高感度化を実現した電子スピン共振装置です。電子状態を間接・直接的に評価、さまざまな応用分野にて研究・開発・検査・評価のサポートを行います。

### 30%アップの高感度化を実現！\*1

試料中の極微量の不安電子が素材の機能を大きく左右することが明らかになりつつある現在、ESR計測は更なる高感度化を求められています。JEOLは、低雑音ガン発振器を改良し従来比30%アップの高感度化を実現しました。



BRUKER 製品とソリューション アプリケーション サービス ニュースとイベント キャリア 企業情報

## ELEXSYS

ELEXSYS-II ESR分光計シリーズは、ライフサイエンス、材料科学、量子コンピューティングのための優れた性能と柔軟性を提供する研究用プラットフォームです。



# Magnetic refrigeration

## Many attempts for commercial use

**Cambridge** Clean, Green & Magnetic

Using novel metal alloys and magnetic fields Cambridge is creating a new generation of low carbon cooling products that will dramatically reduce energy consumption and use no polluting gases.

Cambridge was selected as part of the Cleantech 100 - one of the top 100 private European clean technology companies.

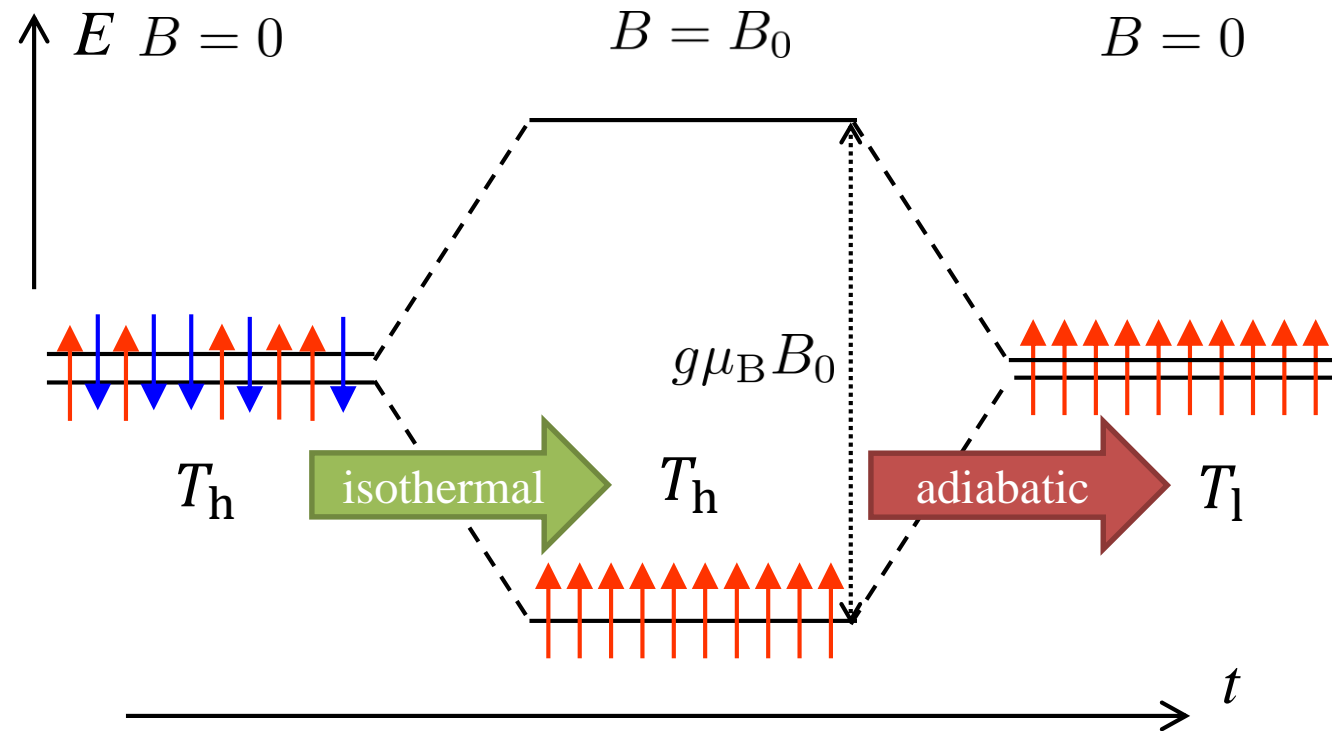
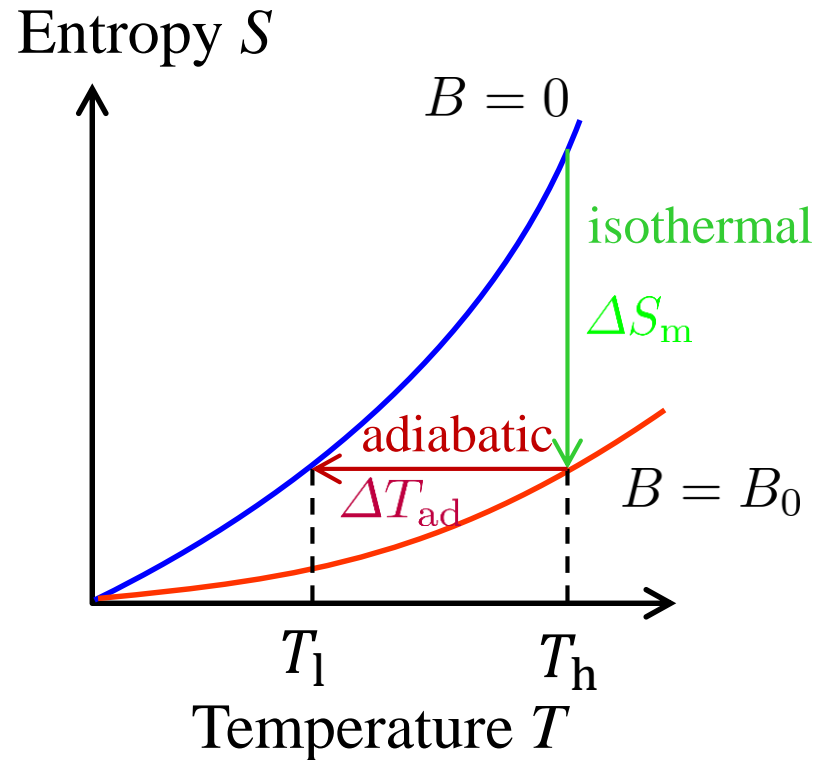
Cleantech 100 AWARD WINNER EVC

EUROPEAN VENTURE CONTEST 2011/12 3-7 December 2012

### Air Conditioning with Magnetic Refrigeration

- Building Efficiency
- Efficiency

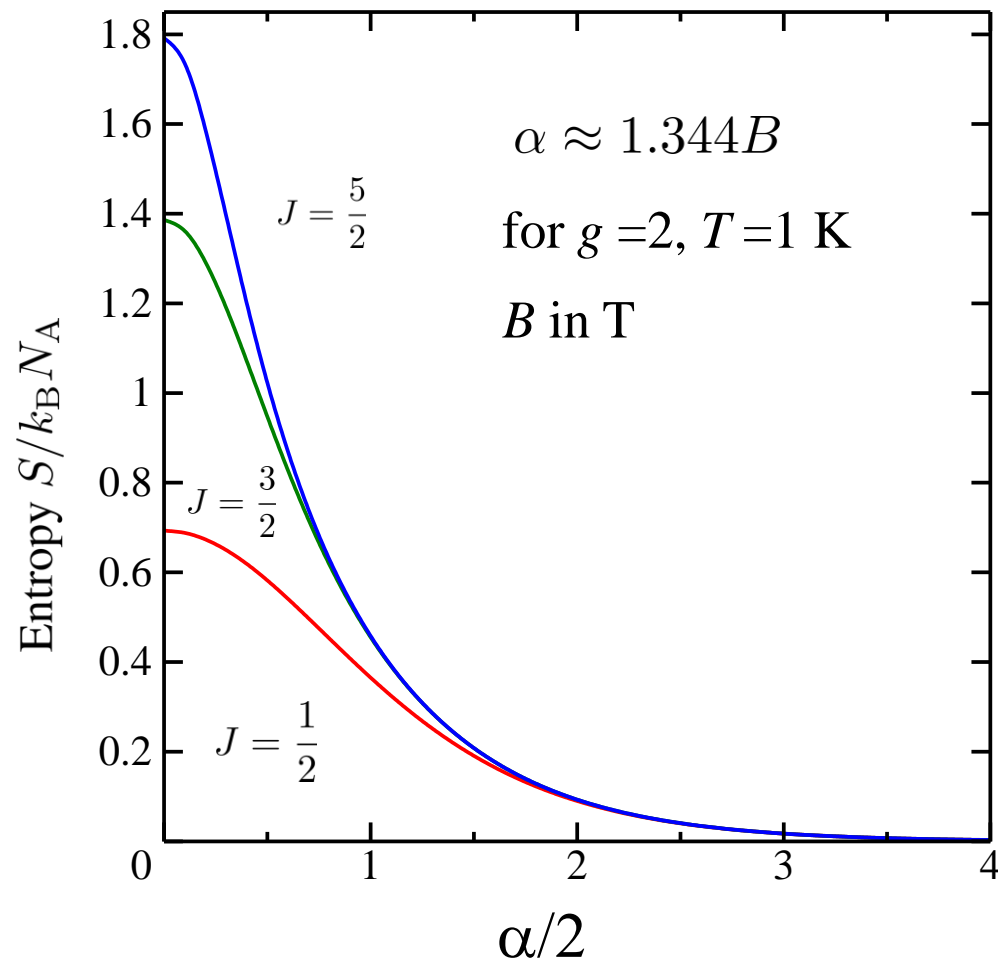
PRINT





# Magnetic refrigeration (2)

Entropy of a free spin system



$$\Delta S(B, T_i) = S(0, T_i) - S(B, T_i) = \int_{T_f}^{T_i} \frac{C_m}{T} dT,$$

$$C_m = T \left( \frac{\partial S}{\partial T} \right)_{B=0}$$

$$M = N_A g \mu_B \left[ \frac{2J+1}{2} \coth \left( \frac{2J+1}{2} \alpha \right) - \frac{1}{2} \coth \frac{\alpha}{2} \right]$$

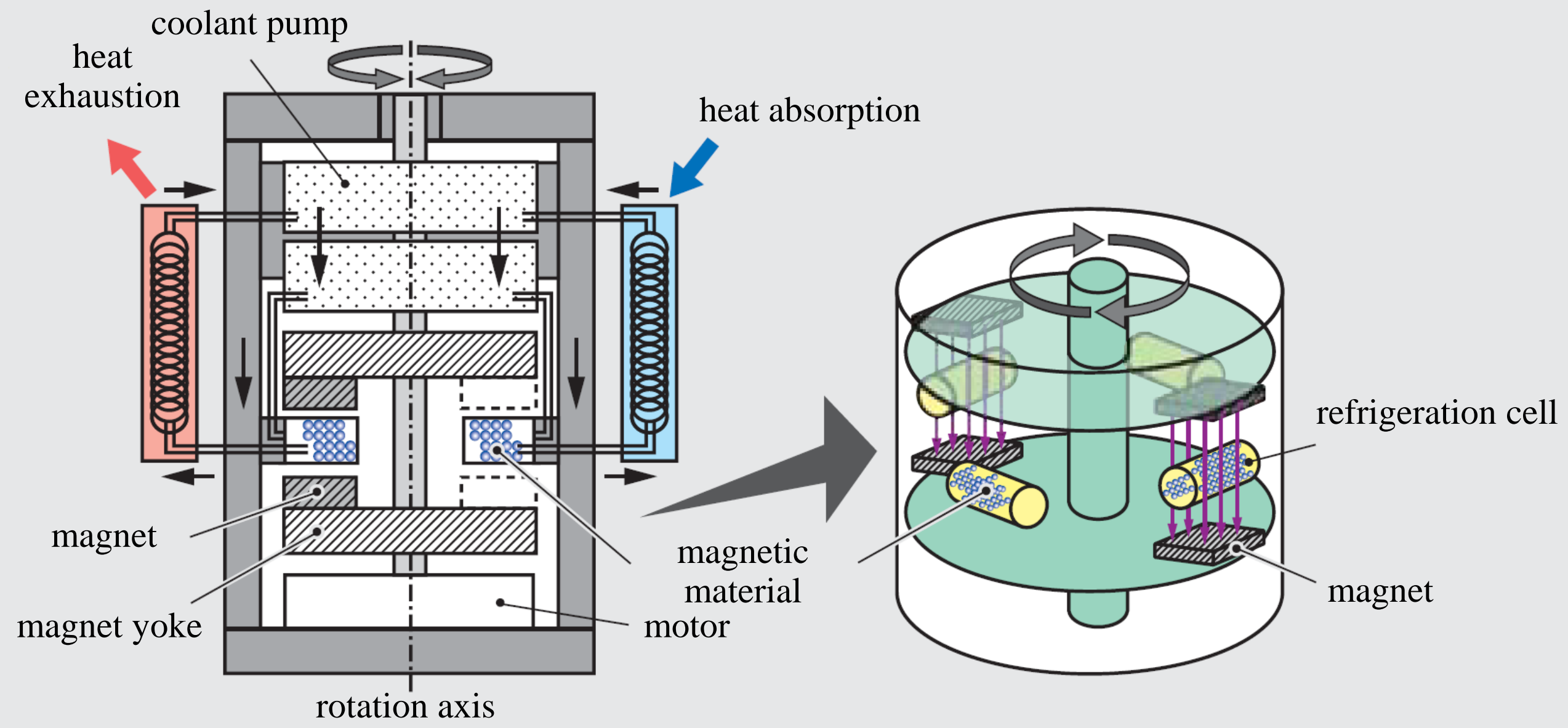
$$\alpha \equiv \frac{g \mu_B B}{k_B T}$$

$$\frac{S}{N_A k_B} = \frac{\alpha}{2} \coth \frac{\alpha}{2} - \frac{2J+1}{2} \alpha \coth \left[ \frac{2J+1}{2} \alpha \right] + \ln \left[ \frac{\sinh[(2J+1)\alpha/2]}{\sinh \alpha/2} \right].$$

Cooling material

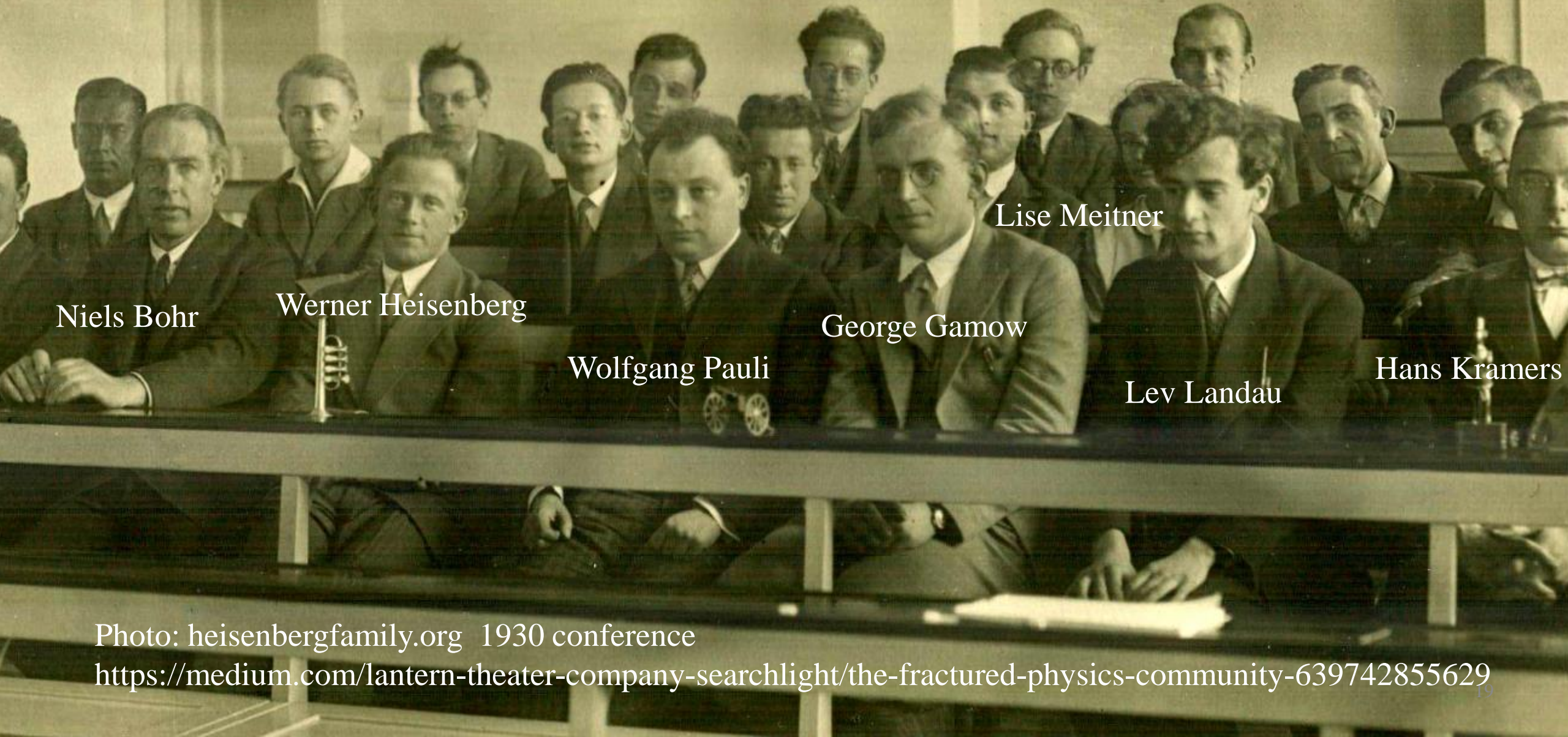
Maxwell relation:  $\left( \frac{\partial S}{\partial B} \right)_T = \left( \frac{\partial M}{\partial T} \right)_B$

# Active magnetic refrigeration





# Chapter 3 Magnetism of Conduction Electrons



Niels Bohr

Werner Heisenberg

Wolfgang Pauli

George Gamow

Lev Landau

Hans Kramers

Lise Meitner

Photo: heisenbergfamily.org 1930 conference

<https://medium.com/lantern-theater-company-searchlight/the-fractured-physics-community-639742855629>

# Chapter 3 Magnetism of Conduction Electrons

3.1 Pauli paramagnetism

3.2 Landau diamagnetism

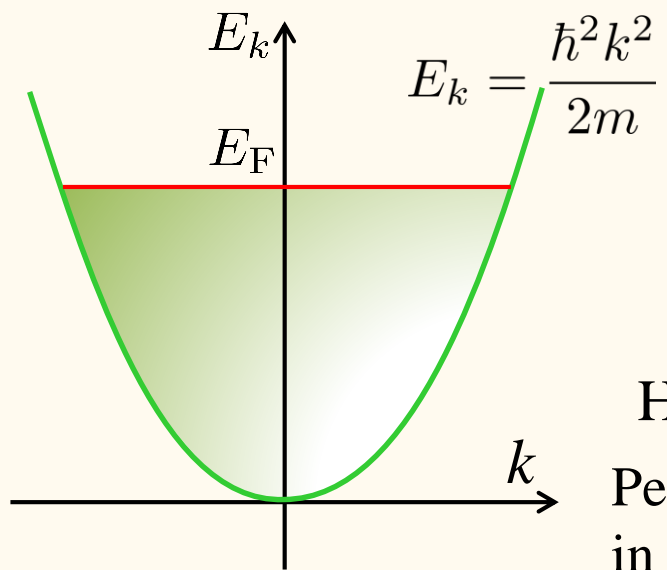
3.3 An example of orbital diamagnetism



<https://sci-toys.com/scitoys/scitoys/magnets/pyrolytic>



# Spin paramagnetism in free electrons



Hamiltonian: kinetic energy + spin  
spin variable:

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} E_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \frac{1}{2} g \mu_B B \sum_{\mathbf{k}\sigma} \sigma c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$$

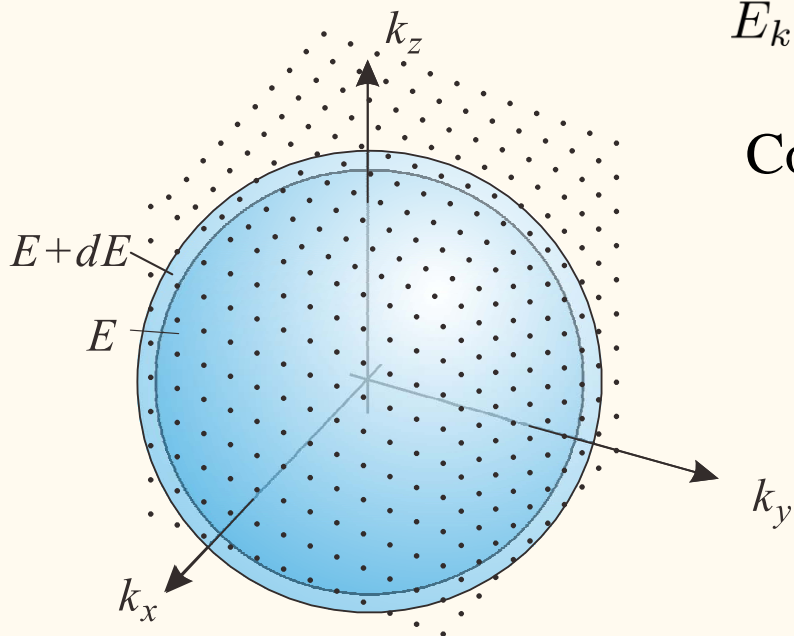
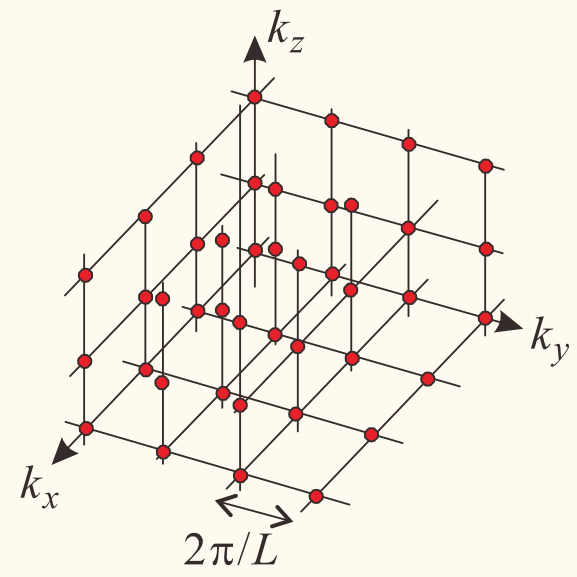
$$\sigma : (\uparrow, \downarrow) \rightarrow (1, -1)$$

How to count  $k$  in metals?  
Periodic boundary condition in  $L$ -cube

$$\mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z) \quad (n_x, n_y, n_z : \text{integers})$$

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

Constant  $E$  sphere radius:  $k_E = \frac{\sqrt{2mE}}{\hbar}$



$$\rho(E) = \frac{1}{L^3} \left( \frac{L}{2\pi} \right)^3 4\pi k_E^2 \frac{dk_E}{dE}$$

$$= \frac{1}{\pi^2 \hbar^3} \sqrt{\frac{mE}{2}}$$

(a)

(b)

# Pauli paramagnetism

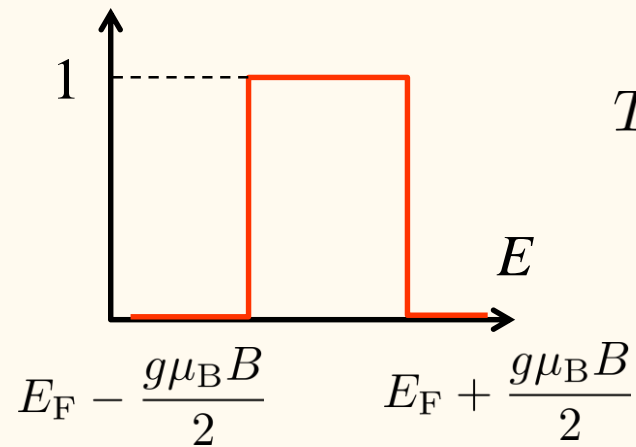
Expectation value of magnetic moment: 
$$-\frac{g\mu_B}{2} \sum_{\mathbf{k}\sigma} \sigma \langle c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} \rangle = \frac{g\mu_B}{2} \sum_{\mathbf{k}} \left[ f \left( E_{\mathbf{k}} - \frac{g\mu_B B}{2} \right) - f \left( E_{\mathbf{k}} + \frac{g\mu_B B}{2} \right) \right]$$

Fermi distribution function: 
$$f(E) = \frac{1}{\exp[(E - \mu)/k_B T] + 1}$$

Chemical potential  $\mu$  is determined from 
$$N_e = \int_0^\infty dE \rho(E) \left[ f \left( E_{\mathbf{k}} - \frac{g\mu_B B}{2} \right) + f \left( E_{\mathbf{k}} + \frac{g\mu_B B}{2} \right) \right]$$
  
 $\mu \rightarrow E_F$

Magnetization: 
$$M = \frac{g\mu_B}{2} \int_0^\infty dE \rho(E) \left[ f \left( E_{\mathbf{k}} - \frac{g\mu_B B}{2} \right) - f \left( E_{\mathbf{k}} + \frac{g\mu_B B}{2} \right) \right]$$

$T \rightarrow 0$



$$2 \left( \frac{g\mu_B B}{2} \right)$$

Pauli paramagnetic susceptibility

$$\chi_{\text{Pauli}} = \left( \frac{g\mu_B}{2} \right)^2 [2\rho(E_F)]$$

$$\frac{\partial M}{\partial B} \rightarrow$$

# Landau quantization



Hamiltonian free electron +  
magnetic field

$$\mathcal{H} = \frac{1}{2m} \sum_i (\mathbf{p}_i + e\mathbf{A})^2$$

Landau gauge:

$$\mathbf{A} = (0, Bx, 0) \quad \mathbf{B} = \text{rot}\mathbf{A} \\ = (0, 0, B)$$

Schrödinger  
equation:

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} + \left( \frac{\partial}{\partial y} - i\frac{eB}{\hbar}x \right)^2 \right] \psi = E\psi$$

Homogeneous for  $y$  and  $z$

→ Functional form assumption:  $\psi = \exp[i(k_y y + k_z z)]u(x)$

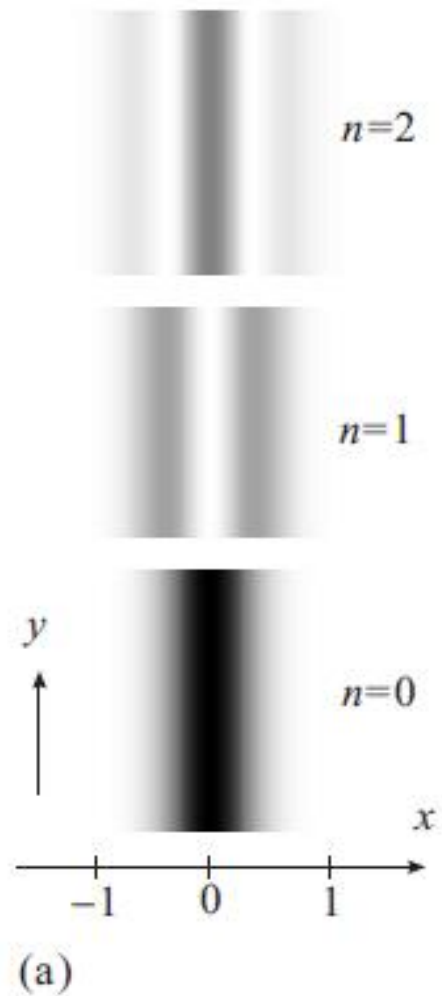
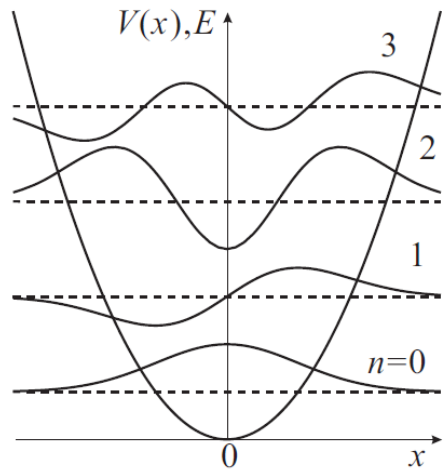
Differential equation for  $x$

$$-\frac{\hbar^2}{2m} \left[ \frac{d^2 u}{dx^2} + \left( k_y - \frac{eB}{\hbar}x \right)^2 u \right] = \left( E - \frac{\hbar^2 k_z^2}{2m} \right) u$$

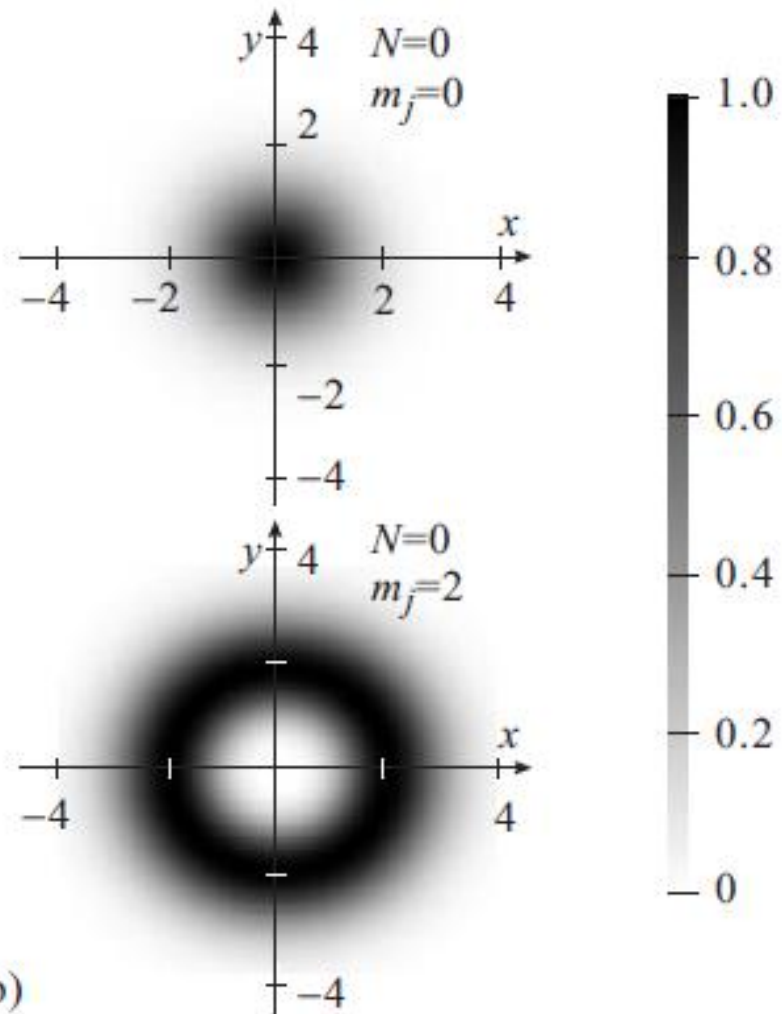
Harmonic oscillator at  $x_c = \frac{\hbar k_y}{eB}$   $\frac{m\omega_c^2}{2} = \frac{(eB)^2}{2m} \quad \therefore \omega_c = \frac{eB}{m}$  : Cyclotron frequency

Landau quantization  $E(n, k_z) = \frac{\hbar^2 k_z^2}{2m} + \left( n + \frac{1}{2} \right) \hbar\omega_c = \frac{\hbar^2 k_z^2}{2m} + (2n + 1)\mu_B B \quad (n = 0, 1, 2, \dots)$

# Landau quantization: forms of wavefunctions



Diagonalize  $X$



Diagonalize  $X^2 + Y^2$  ← Symmetric gauge  
 $\mathbf{A} = \mathbf{B} \times \mathbf{r}/2$



# Orbital diamagnetism

How to count density of states?

Periodic boundary condition in a cube with side length  $L$

$$\text{z-direction} \quad k_z = \frac{2\pi}{L}n_z \quad (n_z = 0, \pm 1, \dots) \quad E_z = \frac{\hbar^2 k_z^2}{2m} \quad \text{Number of } k_z \text{ below } E_z \quad \frac{2L\sqrt{2mE_z}}{h}$$

$$\text{y-direction} \quad k_y = \frac{2\pi}{L}n_y \quad (n_y = 0, \pm 1, \dots)$$

$$\text{x-direction} \quad -\frac{L}{2} \leq x_c \leq \frac{L}{2} \quad -\frac{L}{2} \leq \frac{\hbar}{eB}k_y = \frac{\hbar}{eB} \frac{2\pi}{L}n_y \leq \frac{L}{2} \quad \therefore |n_y| \leq \frac{eBL^2}{4\pi\hbar}$$

Landau level degeneracy (in xy-plane) is  $\frac{eBL^2}{h}$

the number of states below the total energy:  $\Omega(E) = \frac{L^3}{h^2} \sqrt{8meB} \sum_{n=0}^{n_{\max}} \sqrt{E - (2n+1)\mu_B B} \quad n_{\max} = \text{int} \left( \frac{E - \mu_B B}{2} \right)$

$$\text{Free energy: } F = N\mu - 2k_B T \int \frac{d\Omega}{dE} \ln\{1 + \exp[-(E - \mu)/k_B T]\} dE$$

Partial integration

$$\begin{aligned}
 \int \frac{d\Omega}{dE} \ln\{1 + \exp[-(E - \mu)/k_B T]\} dE &= - \int \Omega(E) \left( -\frac{1}{k_B T} \right) \frac{\exp[-(E - \mu)/k_B T]}{1 + \exp[-(E - \mu)/k_B T]} dE \\
 &= \frac{1}{k_B T} \int \left[ \int \Omega(E) dE \right] \frac{d}{dE} \frac{1}{1 + \exp[(E - \mu)/k_B T]} dE \\
 &= \frac{1}{k_B T} \frac{2\sqrt{8m}}{3} \frac{eBL^3}{h^2} \int \sum_{n=0}^{n_{\max}} [E - (2n + 1)\mu_B B]^{3/2} \frac{d}{dE} \frac{1}{1 + \exp[(E - \mu)/k_B T]} dE
 \end{aligned}$$

$$F = N_e \mu - A \int \phi(E) \frac{d}{dE} \frac{1}{1 + \exp[(E - \mu)/k_B T]} dE$$

$$\left\{ \begin{aligned}
 A &= \frac{16L^3}{3\pi^2 \hbar^3} m^{3/2} (\mu_B B)^{5/2}, \\
 \phi(E) &= \sum_{n=0}^{n_{\max}} \left[ \frac{E}{2\mu_B B} - \left( n + \frac{1}{2} \right) \right]^{3/2} \\
 \mu_B &= \frac{e\hbar}{2m}
 \end{aligned} \right.$$

$$T \rightarrow 0 \quad F = N_e E_F - A \phi(E_F)$$

# Orbital diamagnetism (3)

To calculate  $\phi(E) = \sum_{n=0}^{n_{\max}} \left[ \frac{E}{2\mu_B B} - \left( n + \frac{1}{2} \right) \right]^{3/2}$

We use an asymptotic expansion  $x \gg 1 \quad \sum_{n=0}^{n_{\max}} \left[ x - \left( n + \frac{1}{2} \right) \right]^{3/2} \approx \frac{2}{5} x^{5/2} - \frac{1}{16} x^{1/2} + \dots$

which can be obtained by applying Euler-Maclaurin formula to  $F(y) = (x - y)^{3/2}$

$$\sum_{n=0}^{n_0} F(n + 1/2) \approx \int_0^{n_0+1} dy F(y) - \frac{1}{24} [F'(n_0 + 1) - F'(0)] \approx \frac{2}{5} x^{5/2} - \frac{1}{16} x^{1/2}$$

The free energy:  $F = \text{const.} - \frac{L^3}{3} \rho(E_F) (\mu_B B)^2 + \dots$

Landau orbital diamagnetism:  $\chi_{\text{Landau}} = -\frac{2}{3} \rho(E_F) \mu_B^2$

Total susceptibility of free electrons:  $\chi = \chi_{\text{Pauli}} + \chi_{\text{Landau}} = \frac{4}{3} \rho(E_F) \mu_B^2$

# Summary

- Magnetic resonance (continued)
- Spin Hamiltonian
- Example of analyzing experimental data on electron paramagnetic resonance
- Application of paramagnetism: magnetic refrigeration

## Chapter 3 Magnetism of conduction electrons

- Pauli paramagnetism
- Landau diamagnetism