2022.5.18 Lecture 6

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

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Review

- 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 quantization ($\rightarrow$ diamagnetism)

Outline

1. Landau diamagnetism
2. de Haas-van Alphen effect
3. Orbital diamagnetism of graphene, graphite

Chapter 4 Interaction between spins

1. Exchange interaction from Heitler-London approximation

Landau quantization

Hamiltonian free electron + magnetic field $\mathscr{H} = \frac{1}{2m}\sum_i (\boldsymbol{p}_i + e\boldsymbol{A})^2$

Landau gauge: $\boldsymbol{A} = (0, Bx, 0)$ $\boldsymbol{B} = \mathrm{rot}\,\boldsymbol{A} = (0, 0, B)$

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

Harmonic oscillator at $x_\mathrm{c} = \frac{\hbar k_y}{eB}$ $\frac{m\omega_\mathrm{c}^2}{2} = \frac{(eB)^2}{2m}$ $\therefore\ \omega_\mathrm{c} = \frac{eB}{m}$: Cyclotron frequency

Landau quantization $E(n, k_z) = \frac{\hbar^2 k_z^2}{2m} + \left(n + \frac{1}{2}\right)\hbar\omega_\mathrm{c} = \frac{\hbar^2 k_z^2}{2m} + (2n+1)\mu_\mathrm{B} B \quad (n = 0, 1, 2, \cdots)$

Orbital diamagnetism

How to count density of states?

Periodic boundary condition in a cube with side length L

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

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

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

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

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

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

Orbital diamagnetism (2)

Partial integration

$$\int \frac{d\Omega}{dE}\ln\{1+\exp[-(E-\mu)/k_{\mathrm{B}}T]\}dE = -\int \Omega(E)\left(-\frac{1}{k_{\mathrm{B}}T}\right)\frac{\exp[-(E-\mu)/k_{\mathrm{B}}T]}{1+\exp[-(E-\mu)/k_{\mathrm{B}}T]}dE$$

$$= \frac{1}{k_{\mathrm{B}}T}\int\left[\int \Omega(E)dE\right]\frac{d}{dE}\frac{1}{1+\exp[(E-\mu)/k_{\mathrm{B}}T]}dE$$

$$= \frac{1}{k_{\mathrm{B}}T}\frac{2\sqrt{8m}}{3}\frac{eBL^3}{h^2}\int\sum_{n=0}^{n_{\max}}[E-(2n+1)\mu_{\mathrm{B}}B]^{3/2}\frac{d}{dE}\frac{1}{1+\exp[(E-\mu)/k_{\mathrm{B}}T]}dE$$

$$F = N_{\mathrm{e}}\mu - A\int \phi(E)\frac{d}{dE}\frac{1}{1+\exp[(E-\mu)/k_{\mathrm{B}}T]}dE$$

$$\begin{cases} A = \dfrac{16L^3}{3\pi^2\hbar^3}m^{3/2}(\mu_{\mathrm{B}}B)^{5/2}, \\ \phi(E) = \displaystyle\sum_{n=0}^{n_{\max}}\left[\frac{E}{2\mu_{\mathrm{B}}B}-\left(n+\frac{1}{2}\right)\right]^{3/2} \end{cases}$$

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2m}$$

$B \to 0$ $\qquad F = N_{\mathrm{e}}E_{\mathrm{F}} - A\phi(E_{\mathrm{F}})$

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 $x \gg 1$ $$\sum_{n=0}^{n_{\max}} \left[x - \left(n + \frac{1}{2} \right) \right]^{3/2} \approx \frac{2}{5} x^{5/2} - \frac{1}{16} x^{1/2} + \cdots$$

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

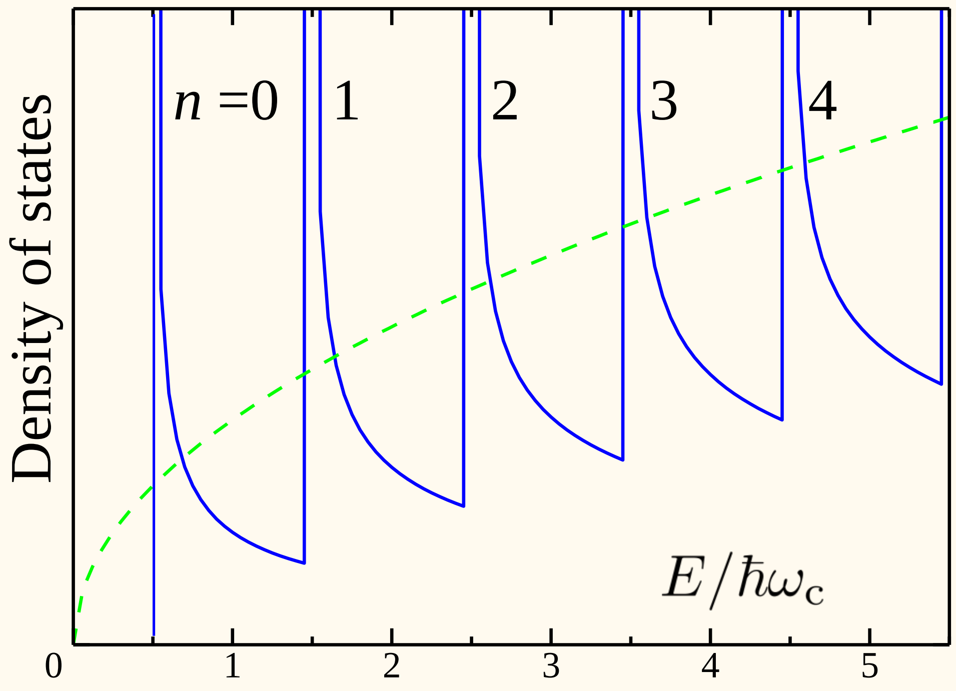
$$\sum_{n=0}^{n_0} F(n+1/2) \approx \int_0^{n_0+1} dy F(y) - \frac{1}{24} [F'(n_0+1) - F'(0)] \approx \frac{2}{5} x^{5/2} - \frac{1}{16} x^{1/2}$$

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

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

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

de Haas-van Alphen effect: orbital magnetization at high magnetic field



Free energy expression

$$\frac{F}{n_e} = \mu - \frac{\hbar\omega_c}{E_F^{3/2}} \int_0^\infty dE \sum_{n=0} \left[E - \left(n + \frac{1}{2} \right) \hbar\omega_c \right]^{3/2} \left(-\frac{\partial f}{\partial E} \right)$$

$$n_e = N_e / L^3$$

Rapid change in the free energy at $(n + 1/2)\hbar\omega_c \approx E_F$

Motion in *z*-direction: Density of states in one-dimensional system

$$E_k = \frac{\hbar^2 k^2}{2m}, \quad \rho_{1d}(E) = \frac{1}{L} \frac{L}{2\pi} \left(\frac{\hbar^2 k}{m} \right)^{-1} = \frac{1}{2\pi\hbar} \sqrt{\frac{m}{2E}}$$

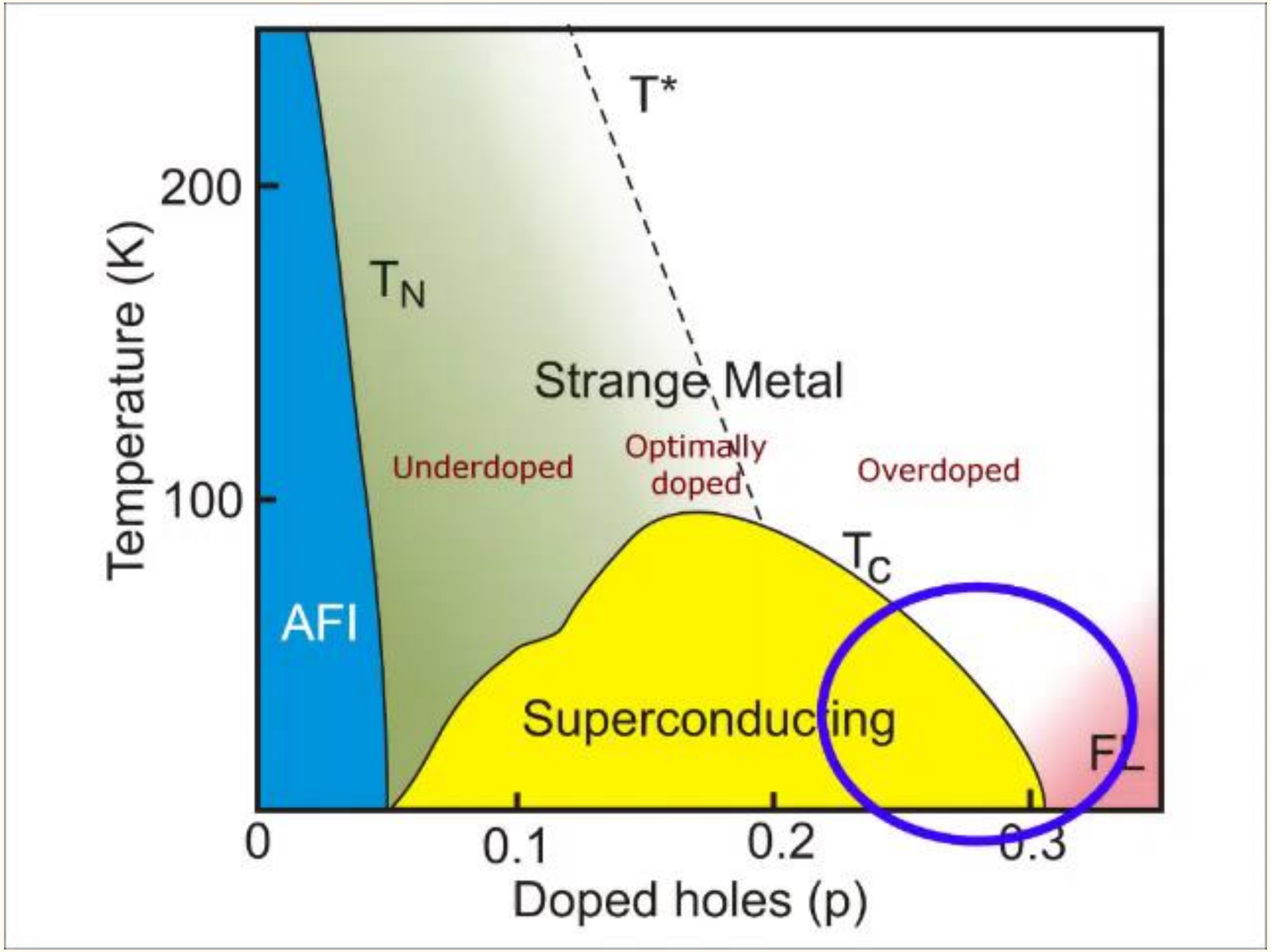
Then the density of states is given by $\rho(E) = \frac{1}{2\pi\hbar} \sqrt{\frac{m}{2}} \sum_{n=0} \frac{1}{\sqrt{(E - (n + 1/2)\hbar\omega_c}}$

Magnetization formula for a spherical Fermi surface

$$M = \frac{e}{4\pi^3} \sum_p \frac{(-1)^p}{p} \int_{-k_F}^{k_F} dk_z \cdot E'_F \sin\left[\frac{p\pi}{\hbar\omega_c} \left(E_F - \frac{\hbar^2 k_z^2}{2m} \right) \right]$$

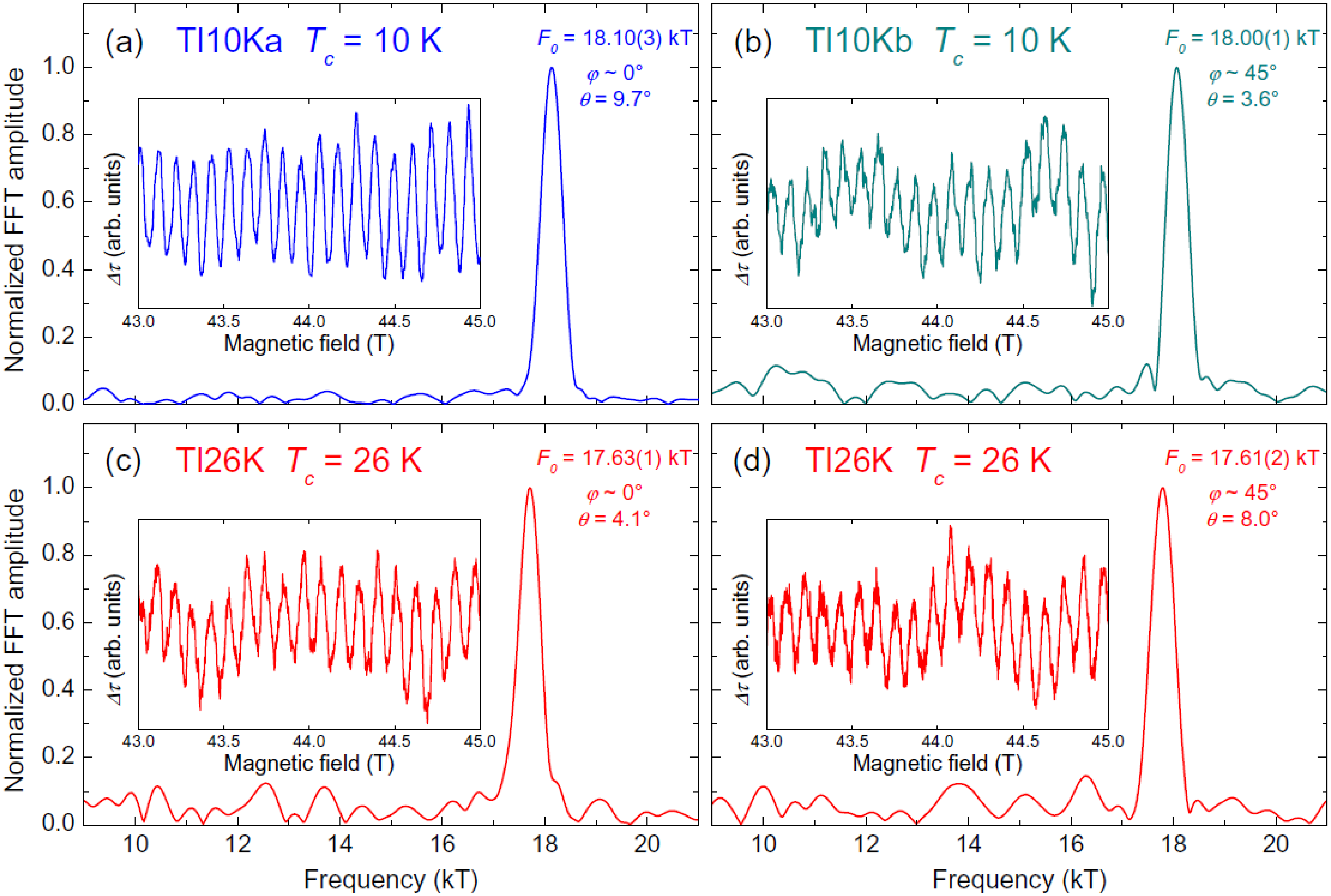
$E'_F = E_F - \frac{\hbar^2 k_z^2}{2m}$ varies slowly compared with the rapidly oscillating sine term other than at around $k_z = 0$

de Haas-van Alphen effect in $Tl_2Ba_2CuO_{6+\delta}$



Rourke et al., New J. Phys. 12, 105009 (2010).

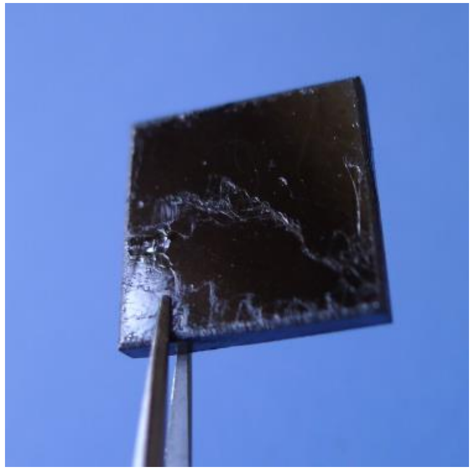
Experimental data on $Tl_2Ba_2CuO_{6+\delta}$



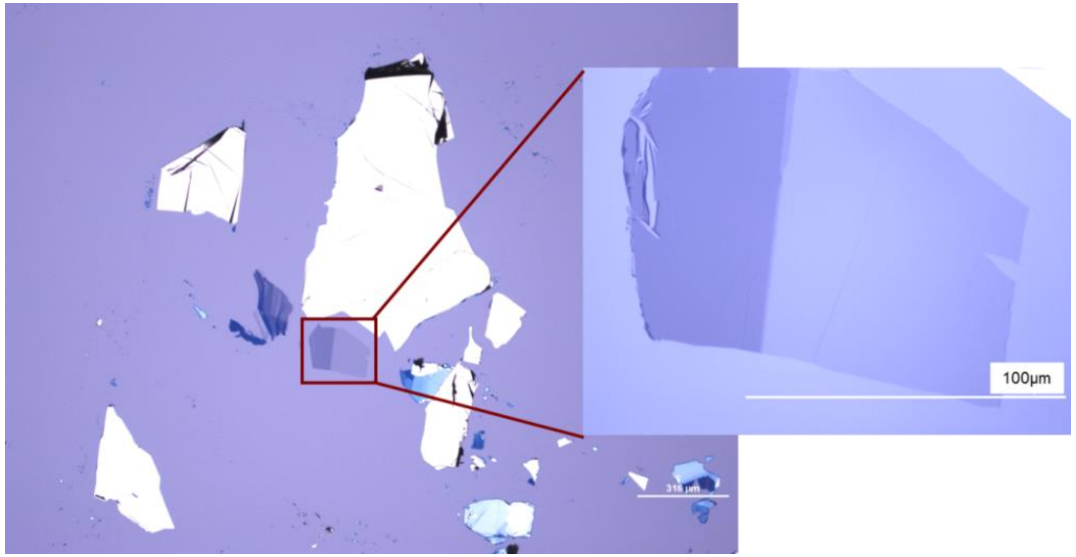
Torque measurement to detect the oscillations in magnetization

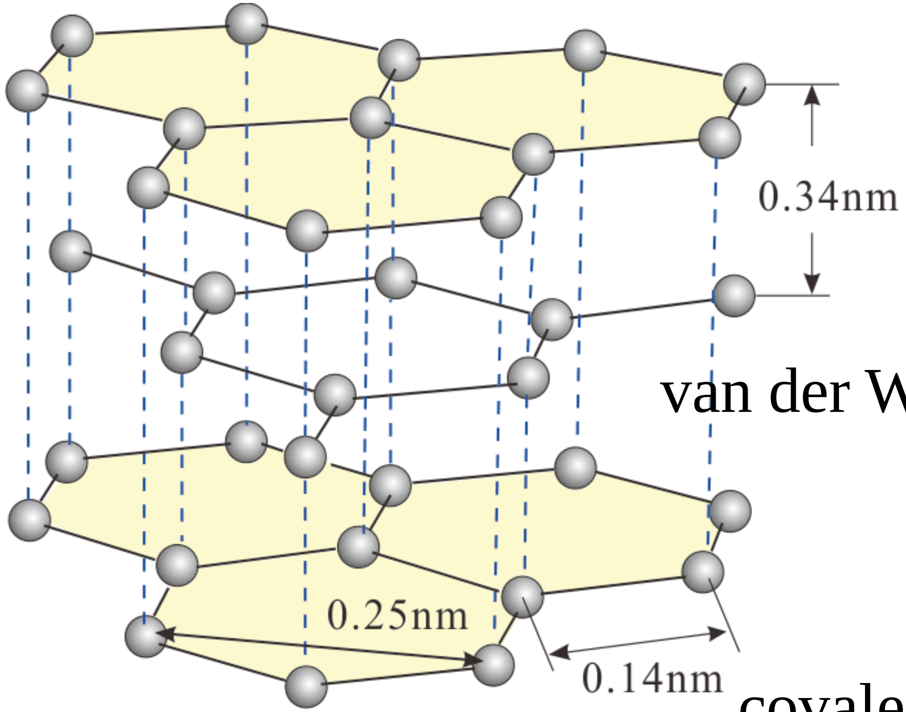
Graphite and Graphene

Graphite



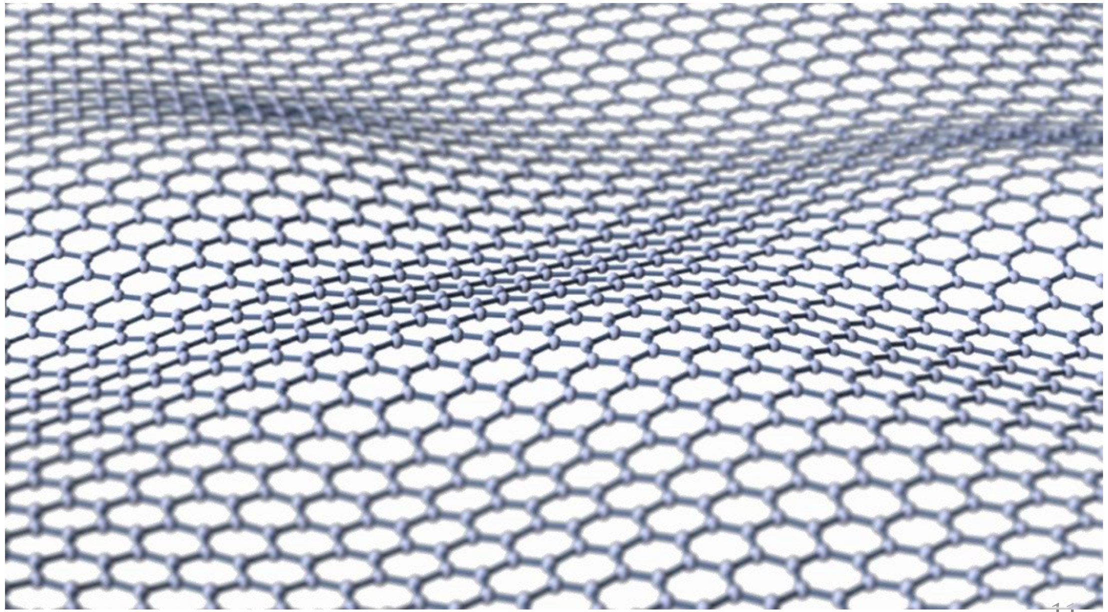
Graphene





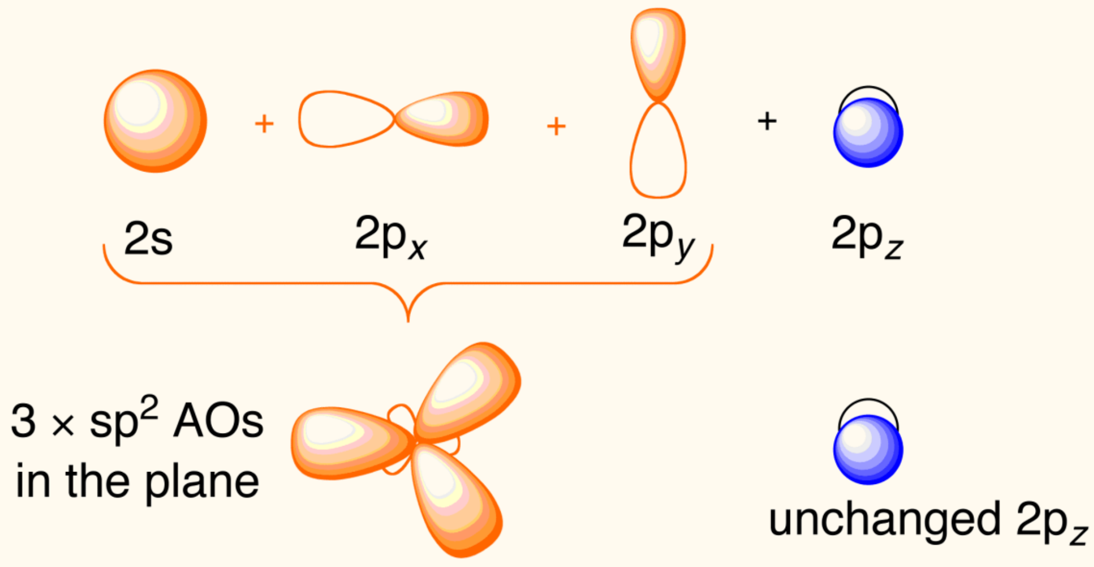
van der Waals

covalent

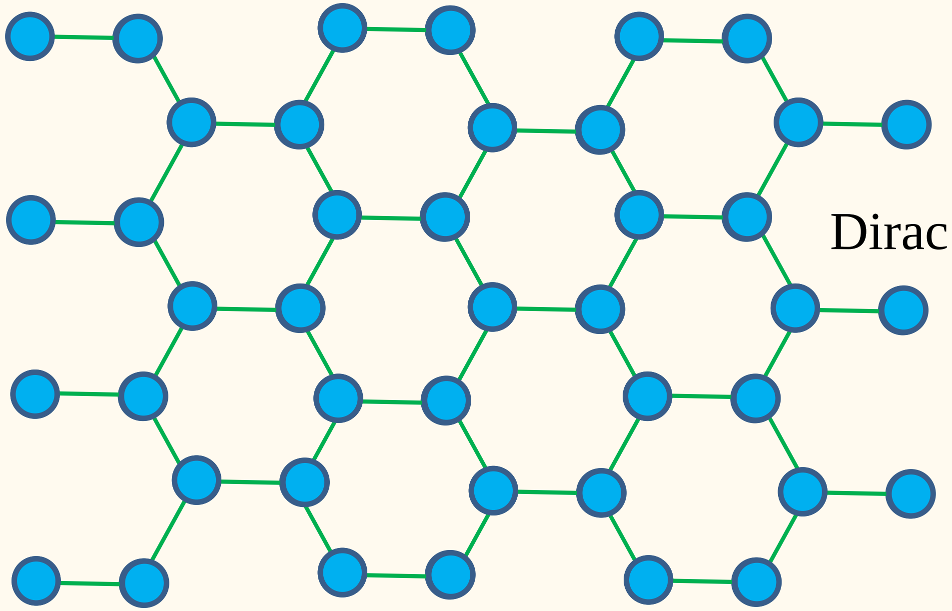


Graphene lattice structure and a simple thought on the band structure

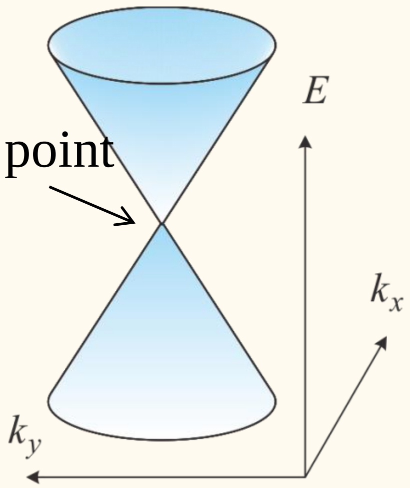
Atomic orbitals



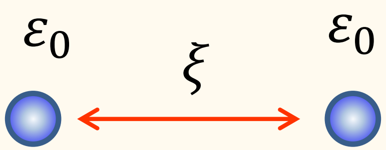
Honeycomb lattice



Dirac corn



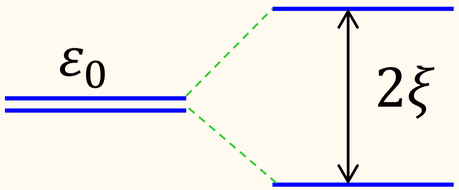
Simple thought on band gap opening



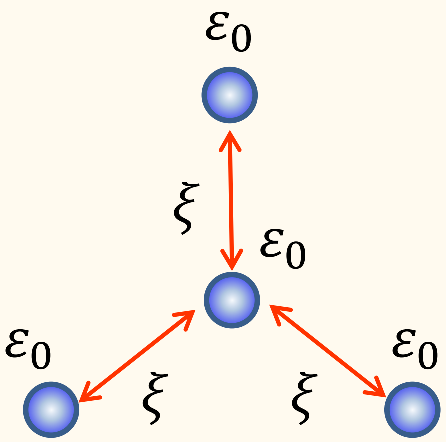
1d nearest neighbor

$$\epsilon = \epsilon_0 \pm \xi$$

$$\mathcal{H} = \begin{pmatrix} \epsilon_0 & \xi \\ \xi & \epsilon_0 \end{pmatrix}$$

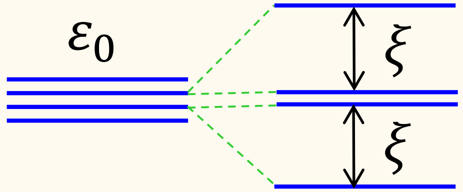


Triangular neighborhood



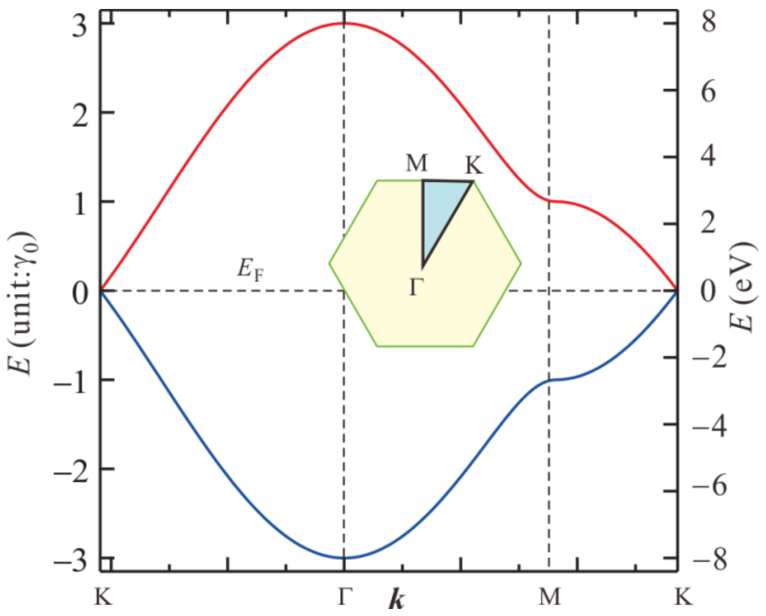
$$\mathcal{H} = \begin{pmatrix} \epsilon_0 & \xi & \xi & \xi \\ \xi & \epsilon_0 & 0 & 0 \\ \xi & 0 & \epsilon_0 & 0 \\ \xi & 0 & 0 & \epsilon_0 \end{pmatrix}$$

$$\epsilon = \epsilon_0(\times 2), \quad \epsilon_0 \pm \xi$$



Degeneracy remains

Graphene band structure: Dirac points in $\boldsymbol{k}$ -space



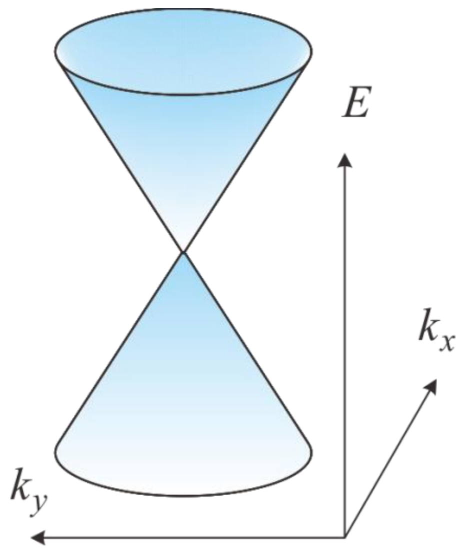
$$E = h_{AA} \pm \xi \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$$

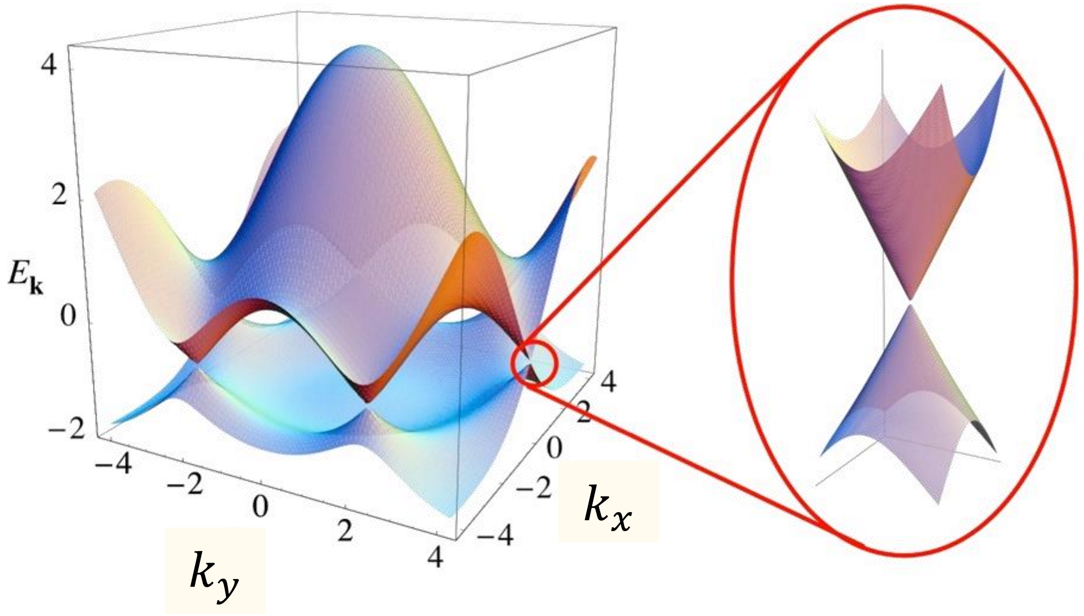
$$k_x = 0$$

$$E = h_{AA} \pm \xi \left|1 + 2\cos\frac{k_y a}{2}\right|$$

$$E\left(k_x, \frac{4\pi}{3a}\right) \approx h_{AA} + \frac{\sqrt{3}\xi a}{2}|k_x|$$

A Dirac point





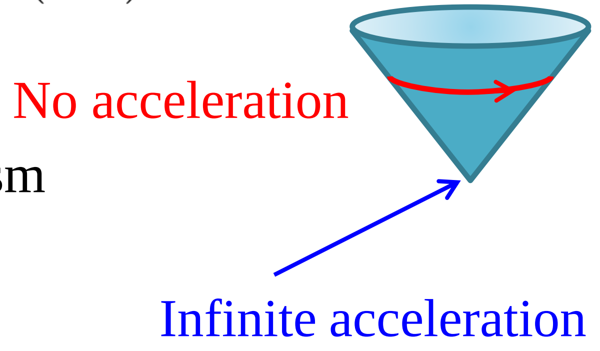
Graphene magnetic susceptibility

$$\chi(E_F) = -\frac{g_v g_s e^2}{6\pi}\left(\frac{e}{c}\right)^2 \delta(E_F)$$

Why this happens?

Remember classical diamagnetism

$$\frac{dL}{dt} = r \times (-eE) = e\frac{r^2}{2}\frac{dB}{dt}$$

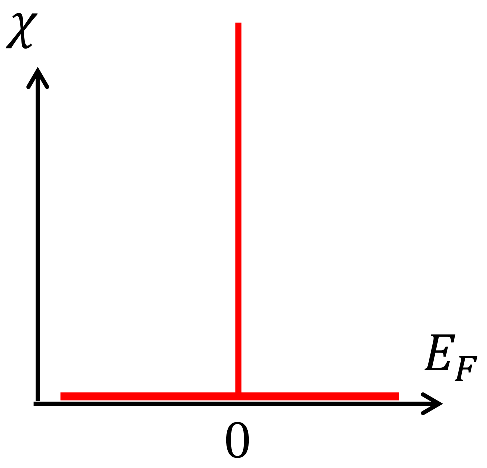


Measurement of graphene diamagnetic susceptibility

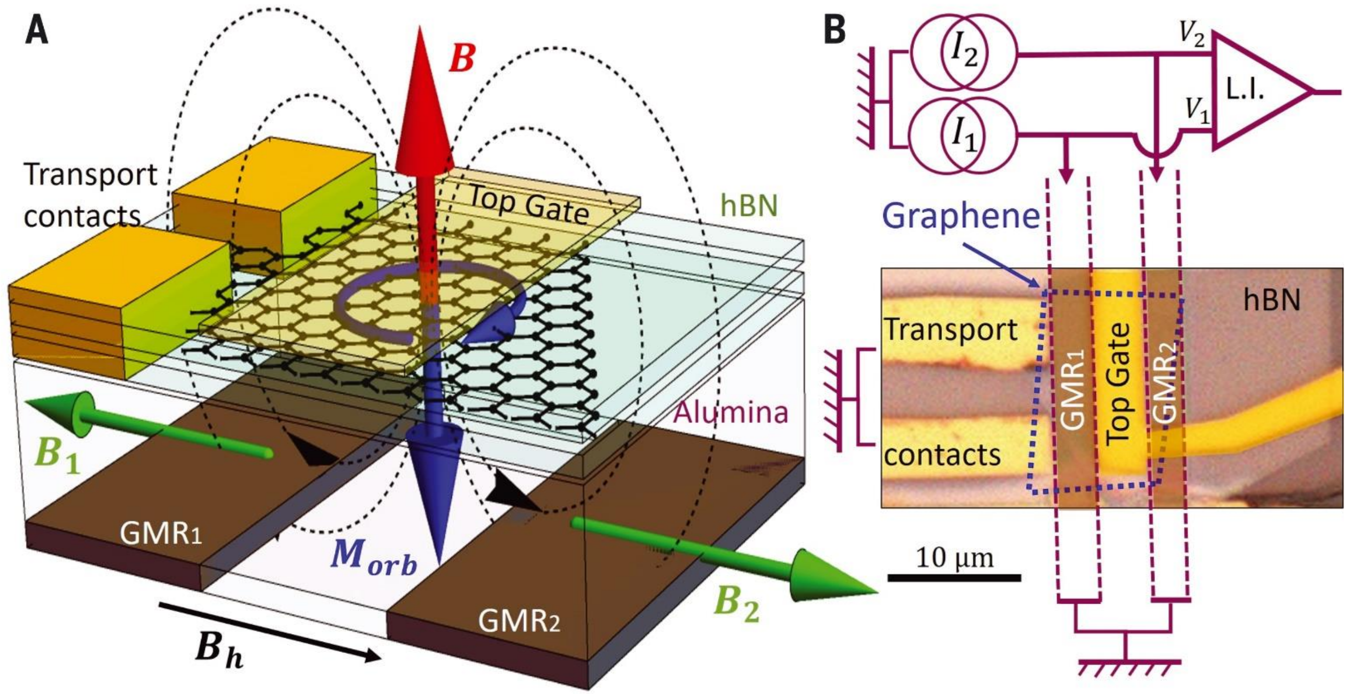
Graphene magnetic susceptibility

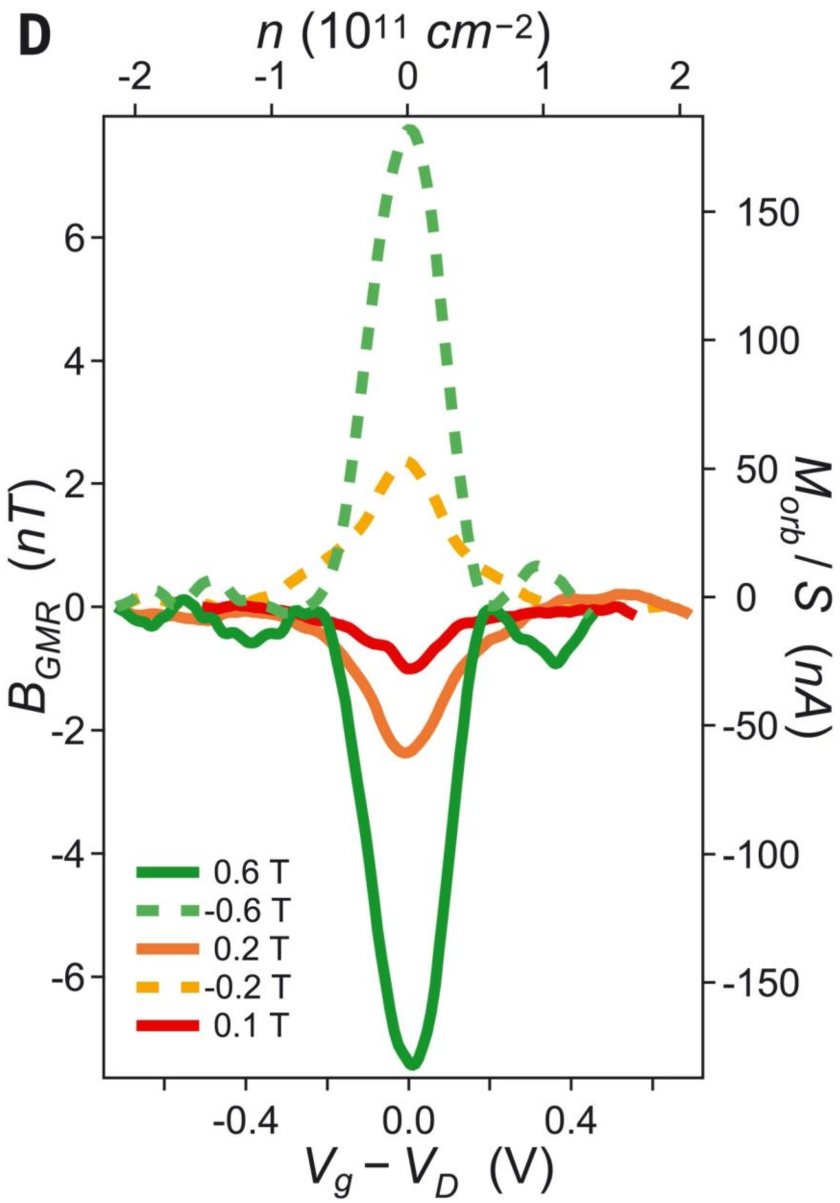
$$\chi(E_{\mathrm{F}}) = -\frac{g_v g_s e^2}{6\pi}\left(\frac{e}{c}\right)^2 \delta(E_{\mathrm{F}})$$

McClure, Phys. Rev. **104**, 666 (1956).

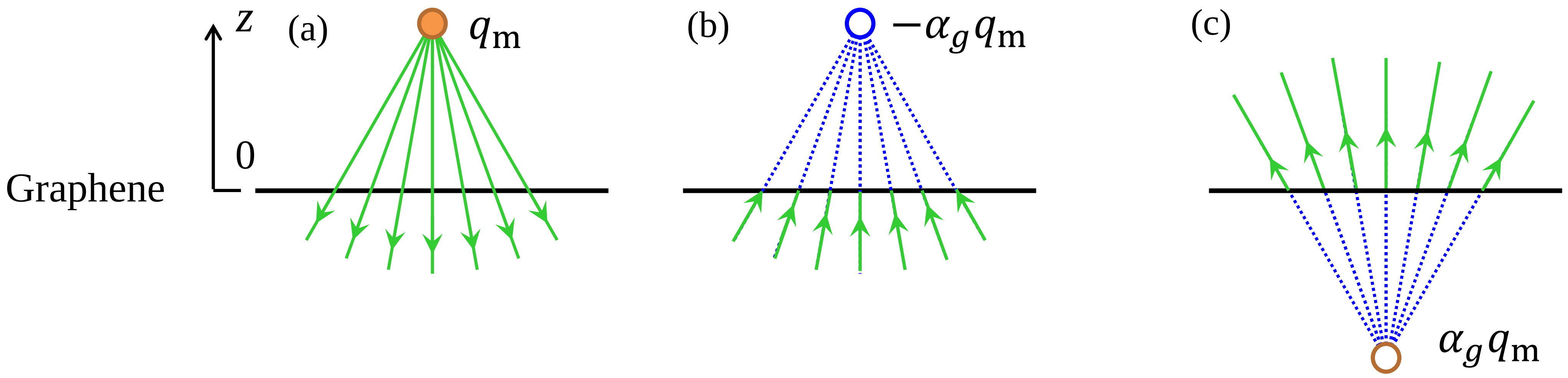


Bustamante et al., Science **374**, 6573 (`21).





Magnetic field screening, repulsion in graphene



Magnetic charge magnetic force line

Virtual charge to express induction field in the region $z < 0$.

Mirror charge to express induction field in the region $z > 0$.

$$B(\boldsymbol{r}) = B(q)\cos qx$$

Magnetic field induced current and magnetization

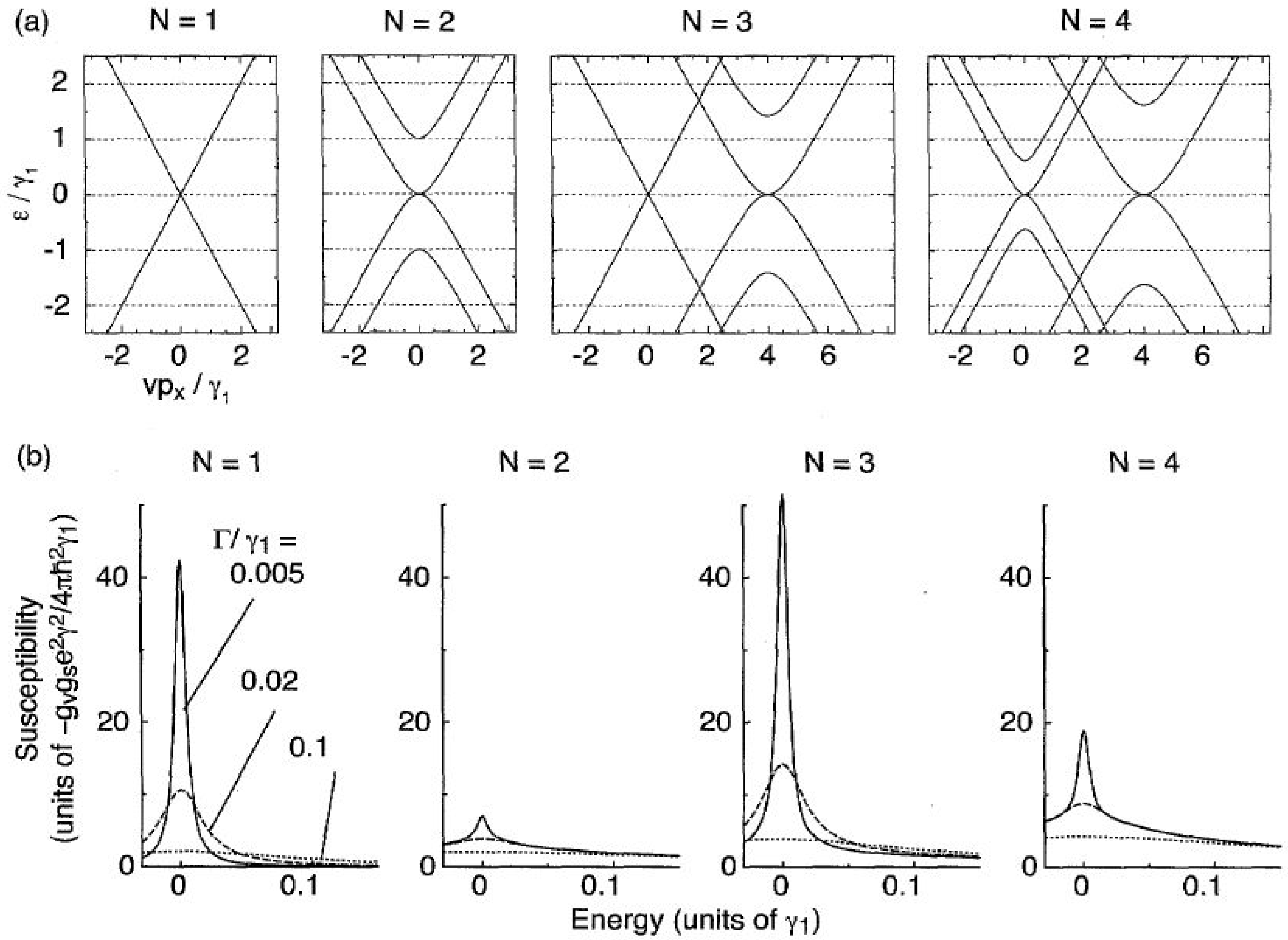
$$j_y = -c\frac{\partial m}{\partial x} \rightarrow m(\boldsymbol{r}) = m(q)\cos qx \quad m(q) = -\frac{j_y(q)}{cq}$$

$$j_y(\boldsymbol{r}) = -\frac{g_v g_s e^2 v}{16\hbar c} B(q)\sin qx$$

$$B_\mathrm{ind}(\boldsymbol{r}) = -\alpha_g B(\boldsymbol{r}), \quad \alpha_g = \frac{2\pi g_v g_s e^2 v}{16\hbar c^2} \approx 4\times 10^{-5}$$

$\sigma_\mathrm{m} \sim 1\ \mathrm{T}$ 0.16 g/cm^2

Multi-layer graphene

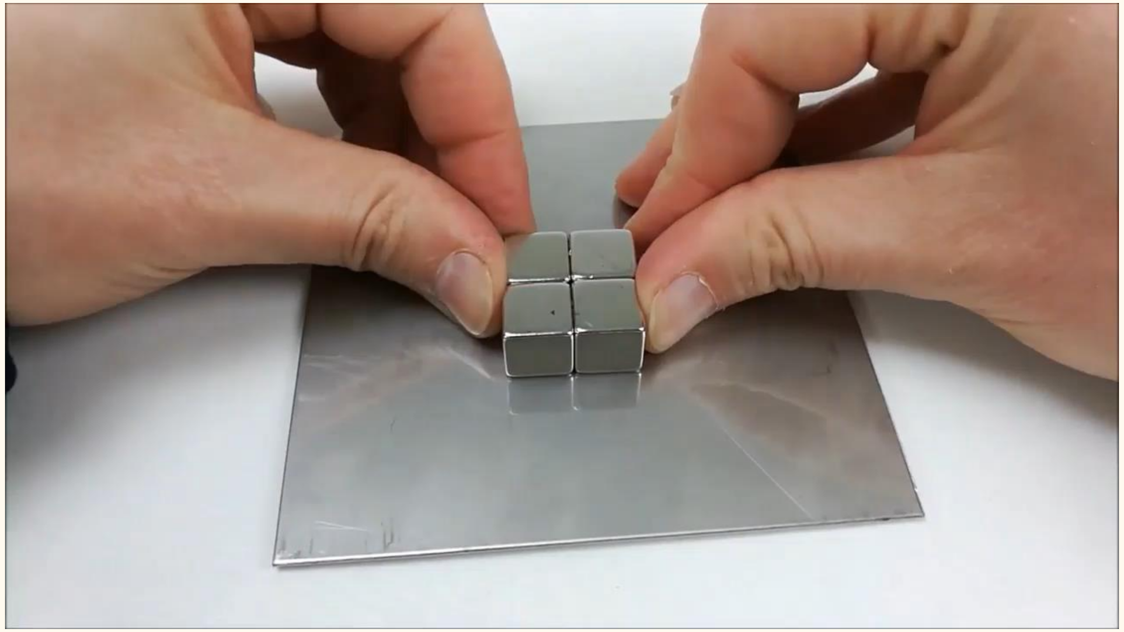


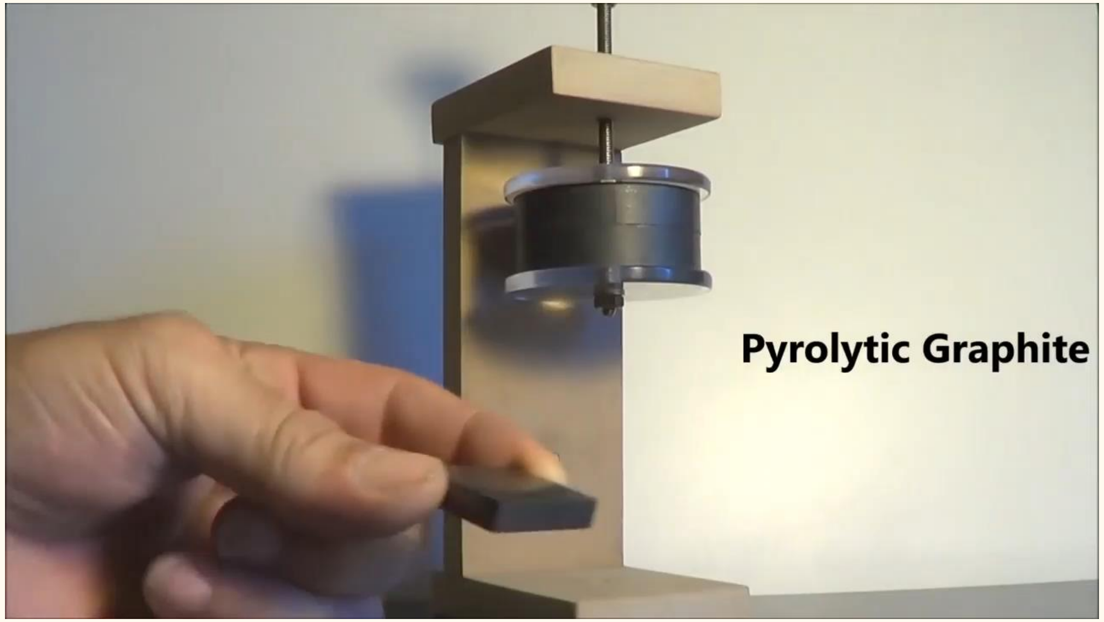
N=2*M*+1 layers

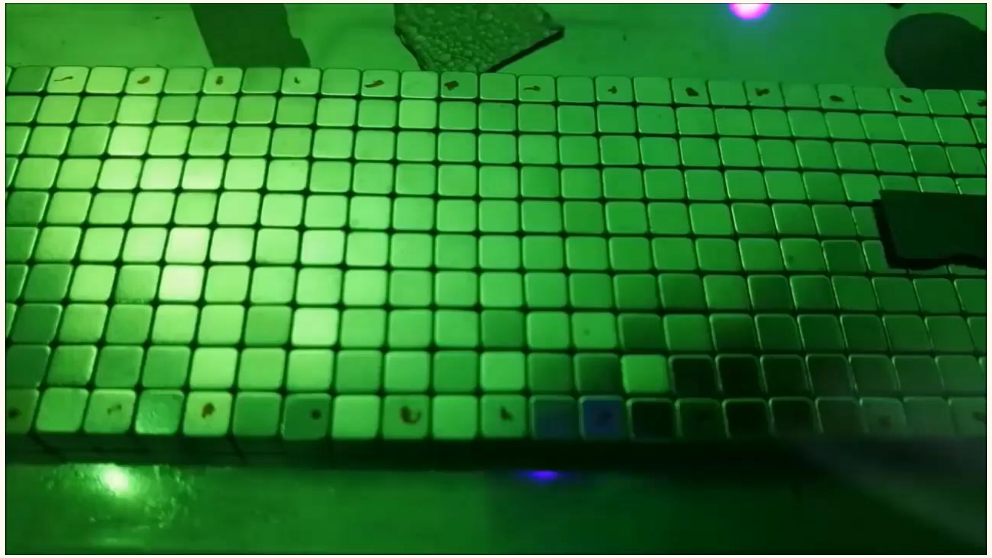
1: Dirac point

M: zero gap+ gapped

Magnetic levitation of graphite







Chapter 4

Interaction between Spins

Chiririn Goma　小泉製作所

Exchange interaction

Classical dipole interaction: $$U(\boldsymbol{\mu}_1, \boldsymbol{\mu}_2, \boldsymbol{r}_{12}) = \frac{\mu_0}{4\pi}\left[\frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r_{12}^3} - 3\frac{(\boldsymbol{r}_1 \cdot \boldsymbol{r}_{12})(\boldsymbol{r}_2 \cdot \boldsymbol{r}_{12})}{r_{12}^5}\right]$$

This cannot explain ferromagnetism $\mu_1 = \mu_2 = 5\mu_{\mathrm{B}}, r_{12} = 0.2\ \mathrm{nm} \rightarrow U \sim 2\ \mathrm{K}$

Quantum mechanical origin of spin-spin interaction: Symmetry of wavefunction

Fermion wavefunction is anti-symmetric: (Orbital part: anti-symmetric) → (Spin part: Symmetric)

If the anti-symmetric orbital part is energetically favorable, this should work as ferromagnetic coupling.

Heitler-London approximation: A two-atom system without hopping

Atomic orbitals: φ_a, φ_b Spin states: χ_a, χ_b

Spin up (α): $\chi(1/2) = 1, \quad \chi(-1/2) = 0$

Spin down (β): $\chi(1/2) = 0, \quad \chi(-1/2) = 1$

Wavefunction Slater determinant

$$\Psi = \frac{1}{\sqrt{N}}\begin{vmatrix} \varphi_a(\boldsymbol{r}_1)\chi_a(s_1) & \varphi_b(\boldsymbol{r}_1)\chi_b(s_1) \\ \varphi_a(\boldsymbol{r}_2)\chi_a(s_2) & \varphi_b(\boldsymbol{r}_2)\chi_b(s_2) \end{vmatrix}$$

Heitler-London approximation

Pauli exclusion: $\Psi(\boldsymbol{r}_1, s_1; \boldsymbol{r}_1, s_1) = 0, \quad \Psi(\boldsymbol{r}_1, s_1; \boldsymbol{r}_2, s_2) = -\Psi(\boldsymbol{r}_2, s_2; \boldsymbol{r}_1, s_1)$

Basis: $\{\Psi_{\alpha\alpha}, \Psi_{\alpha\beta}, \Psi_{\beta\alpha}, \Psi_{\beta\beta}\}$

Example of interaction Hamiltonian calculation:

$$\langle\alpha\alpha|\mathscr{H}_{\text{int}}|\alpha\alpha\rangle = \sum_{s_1,s_2} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \Psi^*_{\alpha\alpha} \mathscr{H}_{\text{int}} \Psi_{\alpha\alpha}$$

$$= \underbrace{\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \varphi^*_a(\boldsymbol{r}_1)\varphi^*_b(\boldsymbol{r}_2)\mathscr{H}_{\text{int}}\varphi_a(\boldsymbol{r}_1)\varphi_b(\boldsymbol{r}_2)}_{K_{ab}} - \underbrace{\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \varphi^*_a(\boldsymbol{r}_1)\varphi^*_b(\boldsymbol{r}_2)\mathscr{H}_{\text{int}}\varphi_b(\boldsymbol{r}_1)\varphi_a(\boldsymbol{r}_2)}_{J_{ab}}$$

J_{ab} Exchange integral

Matrix elements:

	$\alpha\alpha$	$\alpha\beta$	$\beta\alpha$	$\beta\beta$
$\alpha\alpha$	$K_{ab} - J_{ab}$	0	0	0
$\alpha\beta$	0	K_{ab}	$-J_{ab}$	0
$\beta\alpha$	0	$-J_{ab}$	K_{ab}	0
$\beta\beta$	0	0	0	$K_{ab} - J_{ab}$

Spin Hamiltonian

Eigenstates:

$$\left.\begin{array}{c}\Psi_{\alpha\alpha}\\ \frac{1}{\sqrt{2}}(\Psi_{\alpha\beta}+\Psi_{\beta\alpha})\\ \Psi_{\beta\beta}\end{array}\right\}(s_1+s_2=1), \qquad \frac{1}{\sqrt{2}}(\Psi_{\alpha\beta}-\Psi_{\beta\alpha})\ (s_1+s_2=0)$$

Spin triplet

Spin singlet

Spin operators: $\boldsymbol{s}_a$, $\boldsymbol{s}_b$

$$2\boldsymbol{s}_a\cdot\boldsymbol{s}_b=(\boldsymbol{s}_a+\boldsymbol{s}_b)^2-\boldsymbol{s}_a^2-\boldsymbol{s}_b^2=\boldsymbol{S}^2-\boldsymbol{s}_a^2-\boldsymbol{s}_b^2$$

$$\langle\uparrow\uparrow|\boldsymbol{S}^2|\uparrow\uparrow\rangle=S(S+1)=2, \quad \boldsymbol{S}^2|\uparrow\downarrow\rangle=0,$$

$$\boldsymbol{s}_a^2=\boldsymbol{s}_b^2=\frac{1}{2}\left(\frac{1}{2}+1\right)=\frac{3}{4}$$

$$(\uparrow\uparrow)\rightarrow 2\boldsymbol{s}_a\cdot\boldsymbol{s}_b=2-2\times\frac{3}{4}=\frac{1}{2}\implies\frac{1}{2}(1+4\boldsymbol{s}_a\cdot\boldsymbol{s}_b)=+1,$$

$$(\uparrow\downarrow)\rightarrow 2\boldsymbol{s}_a\cdot\boldsymbol{s}_b=2-2\times\frac{3}{4}=-\frac{3}{2}\implies\frac{1}{2}(1+4\boldsymbol{s}_a\cdot\boldsymbol{s}_b)=-1$$

Heisenberg Hamiltonian

Effective Hamiltonian: $\mathscr{H}_{\text{int}} = K_{ab} - \frac{1}{2} J_{ab}(1 + 4\boldsymbol{s}_a \cdot \boldsymbol{s}_b)$ Direct exchange interaction

Heisenberg Hamiltonian: $\mathscr{H} = -2 \sum_{\langle i,j \rangle} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$ Exchange interaction

Exchange integral: $J_{ab} = \frac{e^2}{4\pi\epsilon_0} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \varphi_a^*(\boldsymbol{r}_1)\varphi_b^*(\boldsymbol{r}_2) \frac{1}{r_{12}} \varphi_b(\boldsymbol{r}_1)\varphi_a(\boldsymbol{r}_2)$

Positive → Ferromagnetic interaction

Weak hopping correction. Superposition of $\Psi' = \frac{1}{\sqrt{N'}} \begin{vmatrix} \varphi_a(\boldsymbol{r}_1)\chi_a(s_1) & \varphi_a(\boldsymbol{r}_1)\chi'_a(s_1) \\ \varphi_a(\boldsymbol{r}_2)\chi_a(s_2) & \varphi_a(\boldsymbol{r}_2)\chi'_a(s_2) \end{vmatrix}$

Electron hopping: $\varphi_b\chi_b \to \varphi_a\chi'_a$ $\quad \langle \Psi | \mathscr{H} | \Psi' \rangle \neq 0$

$\boldsymbol{s}_a,\ \boldsymbol{s}_b :$ anti-parallel ⟶ Energy gain $W_{ab} = -\frac{1}{\Delta E} |\langle \Psi' | \mathscr{H} | \Psi \rangle|^2$

$\frac{1}{2}(1 - 4\boldsymbol{s}_a \cdot \boldsymbol{s}_b) W_{ab}$ $\quad \mathscr{H}'_{\text{int}} = \frac{1}{2}(-J_{ab} + W_{ab}) - 2(J_{ab} + W_{ab})\boldsymbol{s}_a \cdot \boldsymbol{s}_b$

Summary

1. Landau diamagnetism
2. de Haas-van Alphen effect
3. Orbital diamagnetism of graphene, graphite

Chapter 4 Interaction between spins

1. Exchange interaction from Heitler-London approximation