# Double Exchange *III*: *Gennes Theory*

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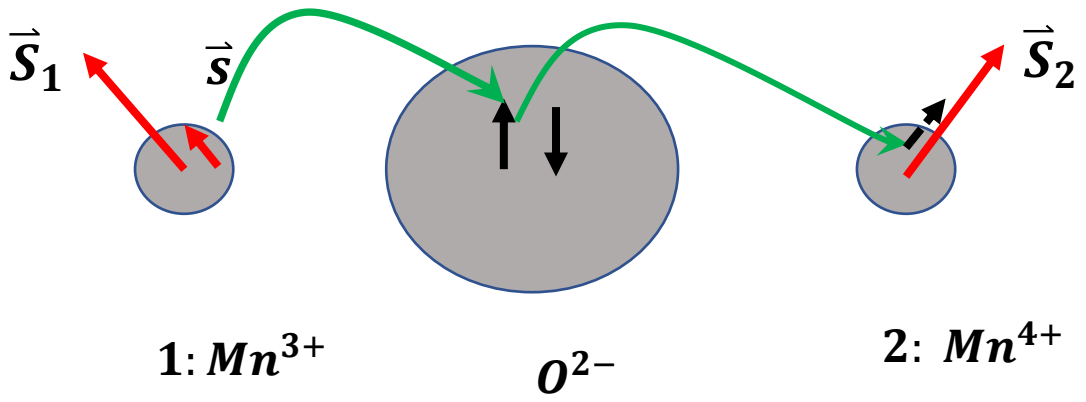
*P.G.de Gennes, Phys. Rev. 118, 141 (1960)*

# *Double Exchange: From Two-ion Case to Antiferromagnetic Lattices*

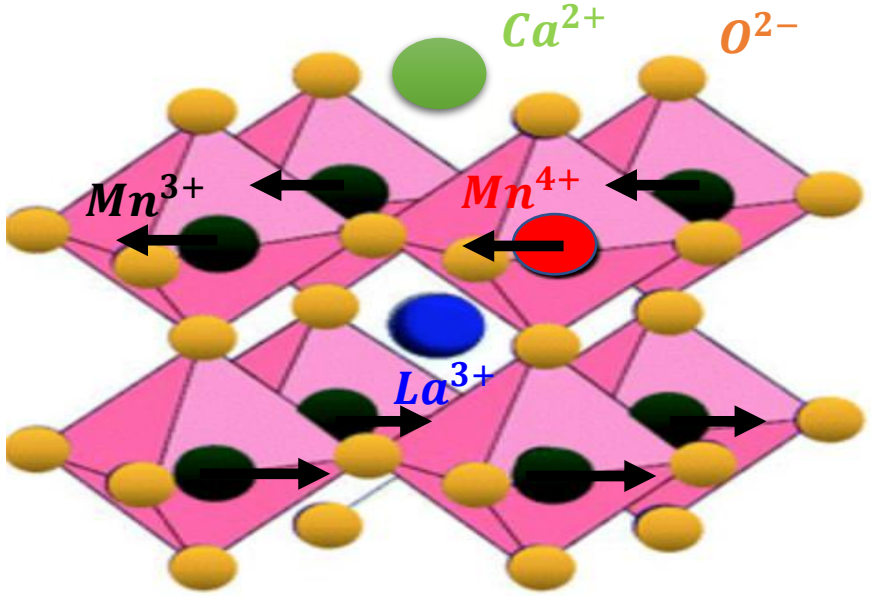
$|R_1\rangle: Mn^{3+}O^{2-}Mn^{4+}$ $\qquad$ $|R_2\rangle: Mn^{4+}O^{2-}Mn^{3+}$




$$\langle \vec{S}_1, \vec{S}_2 \rangle = \theta \qquad \hat{b} = \langle R_1 | \Delta H | R_2 \rangle$$

$$|b|(\sim 0.5 - 1\ eV) \gg kT_c(\sim 0.1 eV)$$

**Ferromagnetic coupling:** $\Delta E_D(\vec{S}_1, \vec{S}_2) = -|b|\ co$




$(La^{3+}_{1-x}Ca^{2+}_{x})(Mn^{3+}_{1-x}Mn^{4+}_{x})O_3$

1. **Electronic states?**
2. **Other exchange interactions?**
3. **Crystal field effects ??**

**…….**

**???**

# *Double Exchange: Outlines*

**Step 1:** *Band Theory* → *Electronic Bloch States* → *Double Exchange Energy*

**Step 2:** *Landau Model* → *Competition between different exchange interactions* → *Spin order: Magnetism ($T = 0$)*

**Step 3:** *Molecular Field Theory* → *Spin order: Magnetism ($T > 0$)* → *Magnetic phase diagram*

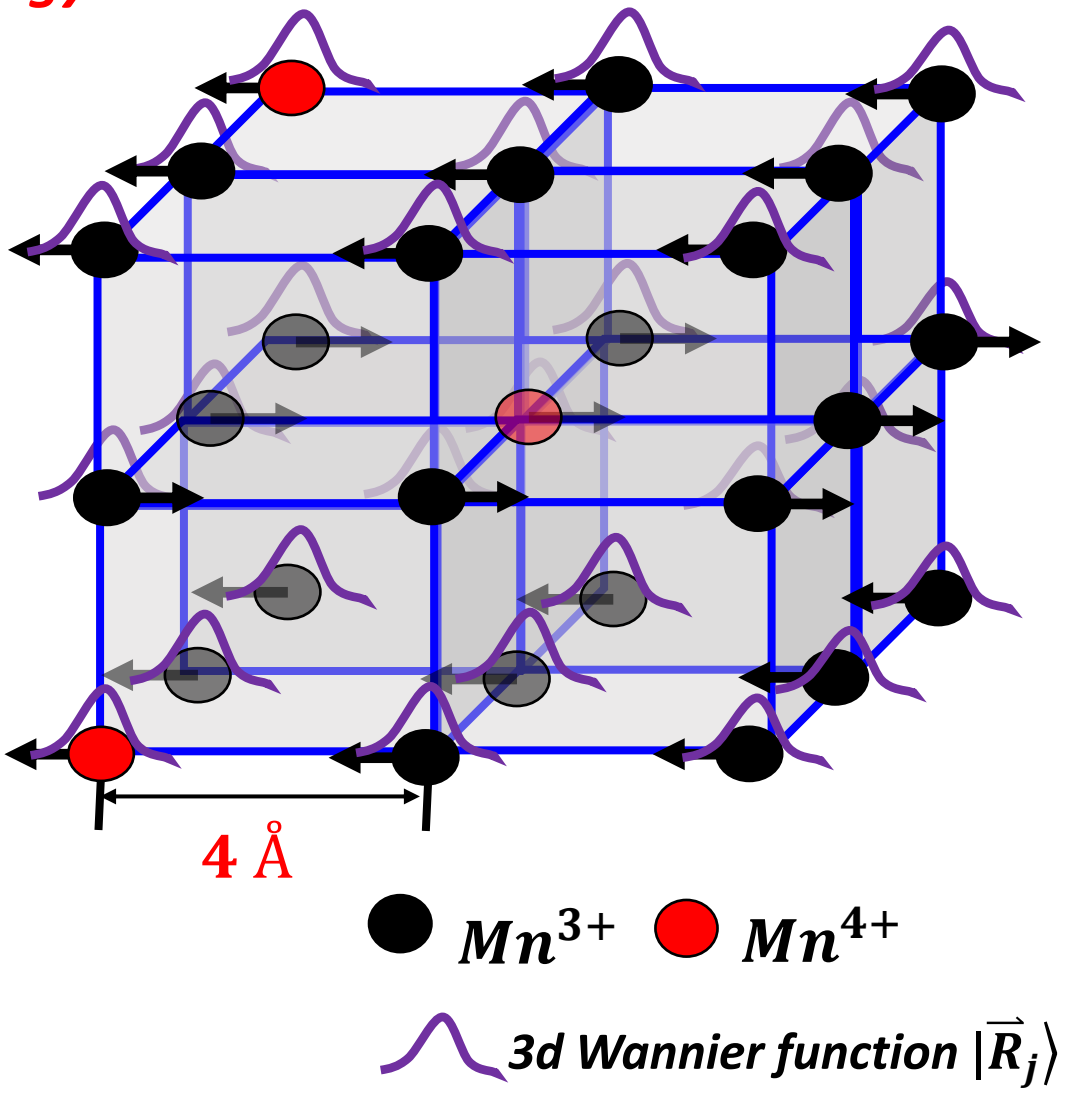
# *Double Exchange: Semiclassical Molecular Field Theory*

## Assumptions:

1. *Tight-binding Approximation: Double exchange energy*

$$\psi_{3d,\vec{k}} = \frac{1}{\sqrt{N}} \sum_{j}^{N} e^{i\vec{k}\cdot\vec{R}_j} |\vec{R}_j\rangle$$

2. *Landau Model: competition between normal exchange and double exchange*
3. *Ignore crystal field effects*
   *Mn 3d band splitting, Mn3d-O2p bonding, Jahn-Teller distortion…*
4. *Non-degenerate 3d-band*
5. *Intra-atomic exchange integral* $\gg b$
6. *Magnetic ion spin* $S_i$ *as classical vectors*
7. *Ignore phonon excitation of ions and Coulomb correlation between carriers*
8. *Ignore bound states of carriers*



# Double Exchange: Semiclassical Molecular Field Theory

## Double exchange energy term

$$1 = \frac{1}{\sqrt{N}}\sum_{j}^{N} |\vec{R}_j\rangle\langle\vec{R}_j|$$

$$(1),\ \psi_{3d,\vec{k}} = \frac{1}{\sqrt{N}}\sum_{j}^{N} e^{i\vec{k}\cdot\vec{R}_j}|\vec{R}_j\rangle \qquad \left\langle\psi_{3d,\vec{k}}\middle|\psi_{3d,\vec{k}'}\right\rangle = \delta_{\vec{k},\vec{k}'}$$

$$(2)\ \Delta H|\psi_{3d,\vec{k}}\rangle = E_{\vec{k}}|\psi_{3d,\vec{k}}\rangle \qquad \langle R_i|\Delta H|R_j\rangle = \hat{b}_{ij}$$

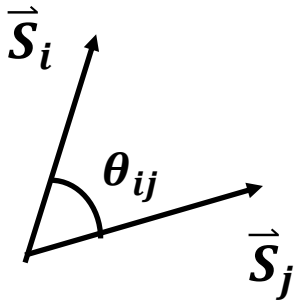
$$\hat{E}_{\vec{k}} = \sum_j^{n.b.} e^{i\vec{k}\cdot(\vec{R}_j-\vec{R}_i)}\hat{b}_{ij}$$

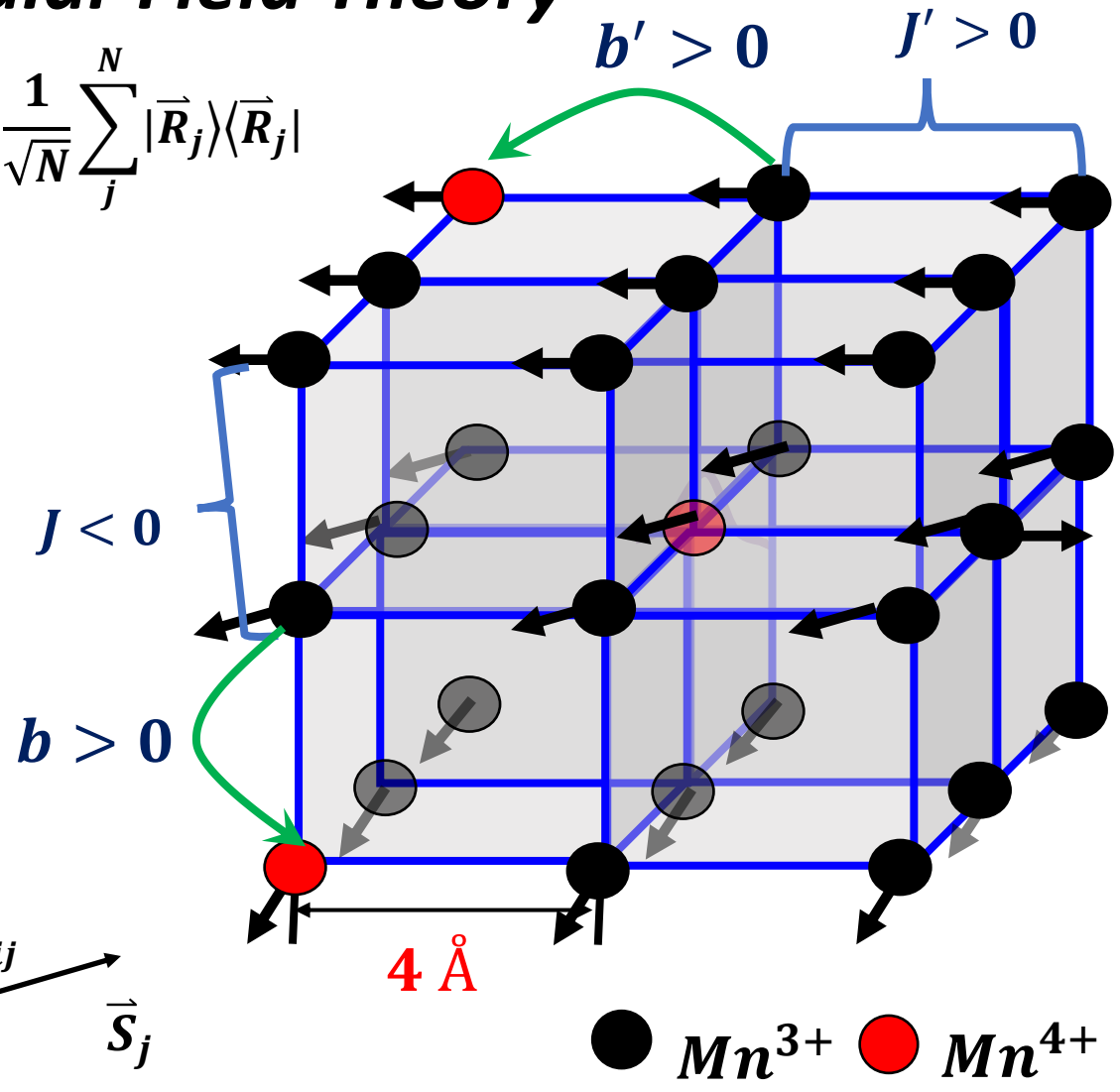
$$(3)\ x \ll 1, \vec{k} = 0 \qquad \hat{E}_{\vec{k}=0} = \sum_j^{n.b.}\hat{b}_{ij}$$

$$(4)\ \textit{Anderson Model}:\ \hat{b}_{ij} \Rightarrow -|b_{ij}|\cos\frac{\theta_{ij}}{2}$$

$$\hat{E}_{\vec{k}=0} = \sum_j^{n.b.}\hat{b}_{ij} \Rightarrow E_{\vec{k}=0} = \sum_j^{n.b.} -|b_{ij}|\cos\frac{\theta_{ij}}{2}$$

$$E_D = NxE_{\vec{k}=0} = -Nxz'b' - Nxzb\cos\frac{\Theta}{2}$$




*$z$, $z'$: nearest neighbors in the same and different layers, respectively; $\Theta$: fixed angle between spins of neighbor layers*

# *Double Exchange: Semiclassical Molecular Field Theory*

| | Two-ion case | Real lattice |
|---|---|---|
| ***Unperturbed Orbital state*** | $\{\lvert R_1\rangle, \lvert R_2\rangle\}$ | Wannier functions $\{\lvert \vec{R}_j\rangle\}$ |
| ***transfer integral*** | $\langle R_1 \lvert \Delta H \rvert R_2\rangle = \hat{b}$ | $\langle R_i \lvert \Delta H \rvert R_j\rangle = \hat{b}_{ij}$ |
| ***Electronic state*** | $\psi_{12} = \frac{1}{\sqrt{2}}[\lvert R_1\rangle \lvert S+\frac{1}{2}, S'_{1z}\rangle - \lvert R_2\rangle \lvert S+\frac{1}{2}, S'_{2z}\rangle]$ | $\Psi_{3d,\vec{k}=0} \approx \prod_j^{n.b.} \otimes \frac{1}{\sqrt{2}}\left[\lvert R_i\rangle \lvert S+\frac{1}{2}, S'_{iz}\rangle - \lvert R_j\rangle \lvert S+\frac{1}{2}, S'_{jz}\rangle\right]$ |
| ***Energy*** | $kT_c \ll \lvert b\rvert$, $-\lvert b\rvert \cos\frac{\theta}{2}$ | $x \ll 1, \vec{k} = 0$ <br> $E_{\vec{k}=0} = -z'b' - zb\cos\frac{\Theta}{2}$ |

***$z$, $z'$: nearest neighbors in the same and different layers, respectively; $\Theta$: fixed angle between spins of neighbor layers; $n.b. \equiv$ nearest neighbors of site $i$, including $i$***

# Double Exchange: Semiclassical Molecular Field Theory

## Other Exchange energy term

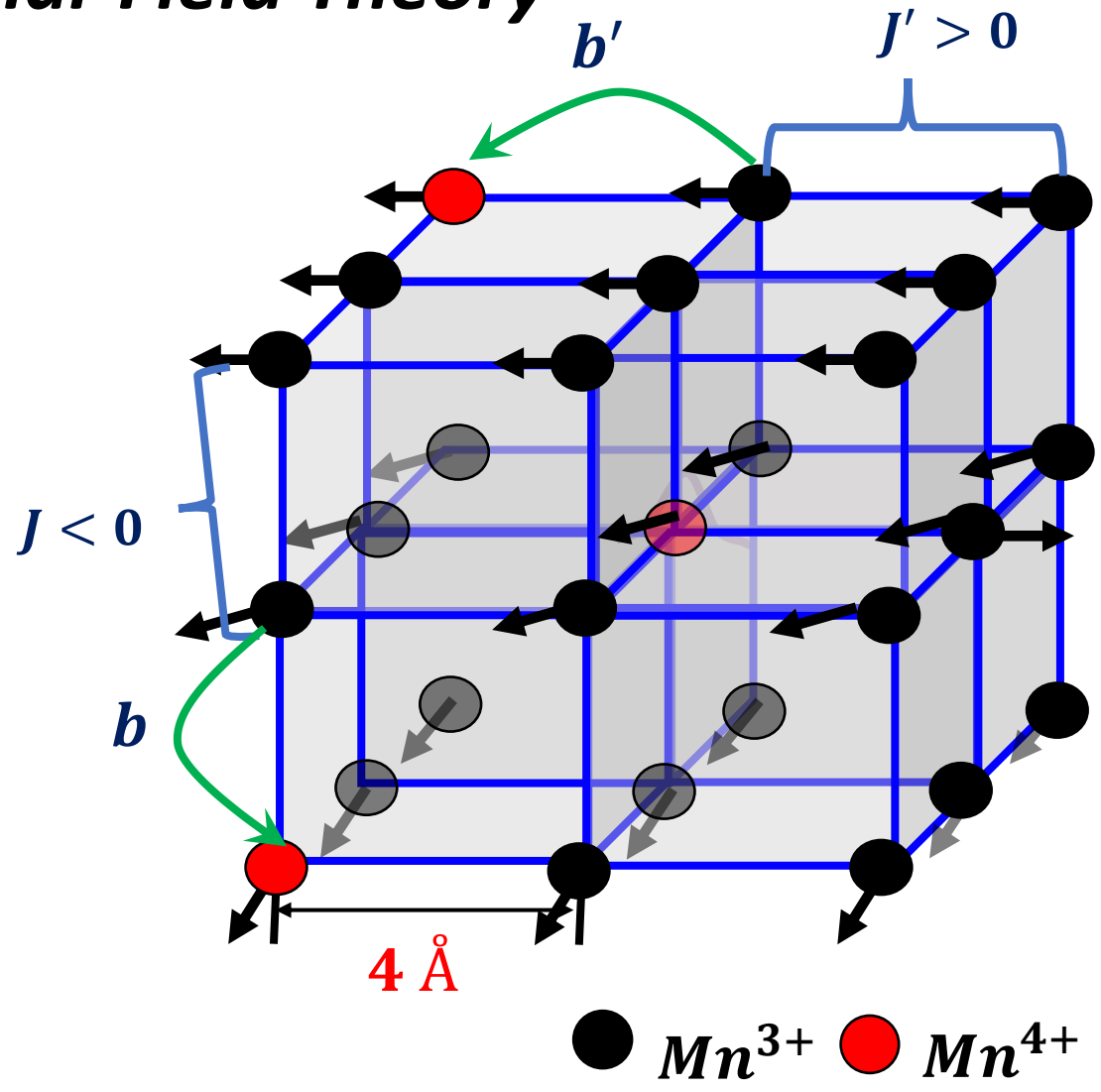
$$E_{ex} = N\left[-\left(z'J'S^2\right) - \left(zJS^2 \cos\Theta\right)\right]$$

## Landau Model

$$E = E_{ex} + E_D = N\left[-\left(z'J'S^2\right) - \left(zJS^2 \cos\Theta\right)\right] - Nxz'b' - Nxzb\cos\frac{\Theta}{2}$$

$$\frac{\delta E}{\delta\Theta} = 0, \frac{\delta^2 E}{\delta\Theta^2} > 0 \quad \Rightarrow \quad \begin{cases} \cos\frac{\Theta}{2} = \frac{bx}{4|J|S^2}, \frac{bx}{4|J|S^2} < 1 \\ \Theta = 0, \quad \frac{bx}{4|J|S^2} \geq 1 \end{cases}$$

$$E = -N\left[z'J'S^2 + xz'b' + z|J|S^2 + \frac{zx^2b^2}{8|J|S^2}\right]$$




*$z$, $z'$: nearest neighbors in the same and adjacent layers, respectively; $\Theta$: fixed angle between spins of neighbor layers*

# *Double Exchange: Potential Experiments*

## Two-sublattice : A stable arrangement

$$\cos\frac{\Theta}{2} = \frac{bx}{4|J|S^2}$$

***(1) Spontaneous Magnetization:***

$$M = I\cos\frac{\Theta}{2}$$

***(2) Isotropic susceptibility in high fields:***

$$E_Z = -HI\cos\frac{\Theta}{2}$$

$$E' = E_Z + E_{ex} + E_D = -HI\cos\frac{\Theta}{2} + N\left[-\left(z'J'S^2\right) - \left(zJS^2\cos\Theta\right)\right] - Nxz'b' - Nxzb\cos\frac{\Theta}{2}$$

$$\frac{\delta E'}{\delta\Theta} = 0, \frac{\delta^2 E'}{\delta\Theta^2} > 0; \quad \cos\frac{\Theta}{2} = \frac{bx}{4|J|S^2} + \frac{HI}{4Nz|J|S^2}$$

$$\chi = -\frac{\partial^2 E'}{\partial H^2} = \frac{I^2}{4Nz|J|S^2}$$

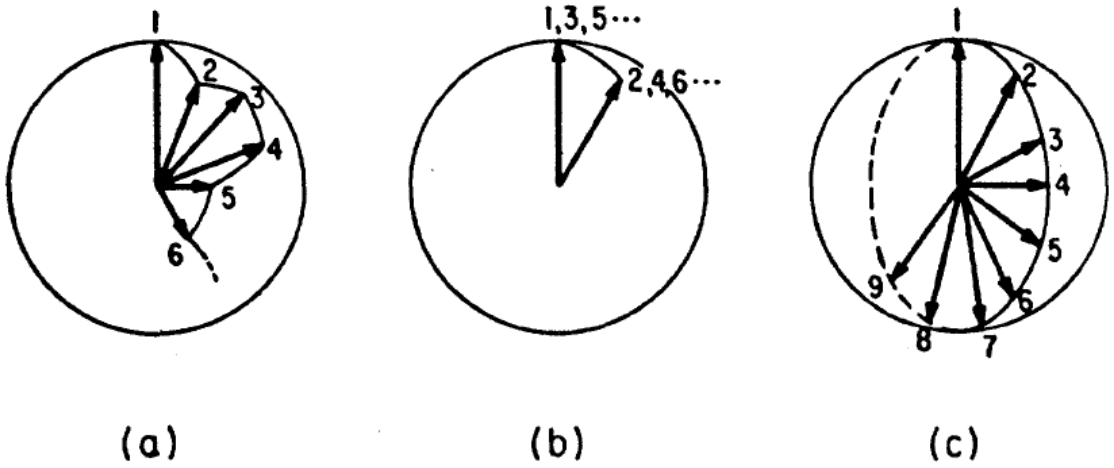


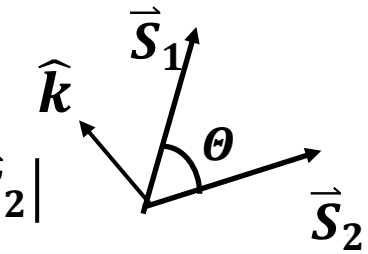

FIG. 1. Allowed configurations for the magnetizations $\mathbf{I}_1, \mathbf{I}_2, \mathbf{I}_3, \cdots, \mathbf{I}_n, \cdots$ corresponding to successive layers. The angle between $\mathbf{I}_n$ and $\mathbf{I}_{n+1}$ is equal to $\Theta_0$. (a) disordered; (b) two sublattice system; (c) helical arrangement. (a), (b), and (c) are degenerate from the standpoint of nearest neighbor exchange and double exchange. External fields, anisotropy energies, or small ferromagnetic couplings between next nearest layers favor configuration (b). Antiferromagnetic coupling between next nearest layers favors (c).

*I. S. Jacobs, J. Phys. Chem. Solids 11, 1. (1959)*

*O. Halpern and M. H. Johnson, Phys. Rev. 55, 898 (1939).*

# Double Exchange: Semiclassical Molecular Field Theory

## Two-sublattice : A stable arrangement




**(3) Neutron diffraction for** $(La^{3+}_{1-x}Ca^{2+}_{x})(Mn^{3+}_{1-x}Mn^{4+}_{x})O_3$

$$S = |\vec{S}_1| = |\vec{S}_2|$$

$$\textit{Scattering Intensity} \propto \left|\vec{u}_{\pm} = \hat{k} \times (\vec{S}_1 \pm \vec{S}_2)\right|^2$$

$\vec{u}_+$: ***"Lattice reflections"(L), in phase***

$\vec{u}_-$: ***"Superlattice reflections"(S), opposite in phase***

$$\hat{k} \perp (\vec{S}_1 \pm \vec{S}_2)$$

$$u^2{}_{ferro} = S^2 cos^2(\Theta/2)$$

$$u^2{}_{antif} = S^2 sin^2(\Theta/2)$$

**Model:** $cos\frac{\Theta}{2} = \frac{bx}{4|J|S^2}$

$$\frac{b}{|J|S^2} \sim 16$$

$$x < 0.25$$

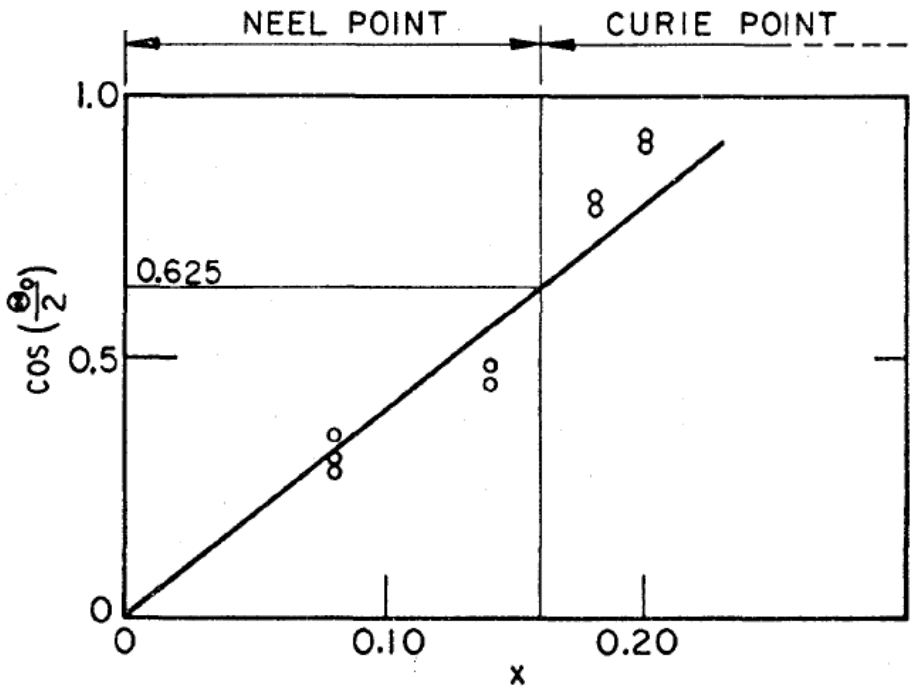



FIG. 3. Determination of the angle $\Theta_0$ between sublattices in the mixed manganites $La_{1-x}Ca_xMnO_3$ with low $Mn^{4+}$ content. The experimental points are deduced from measurements of "ferromagnetic" and "antiferromagnetic" neutron line intensities by Wollan and Koehler.[2] The straight line corresponds to Eq. (9) with $b/|J|S^2 = 16$.

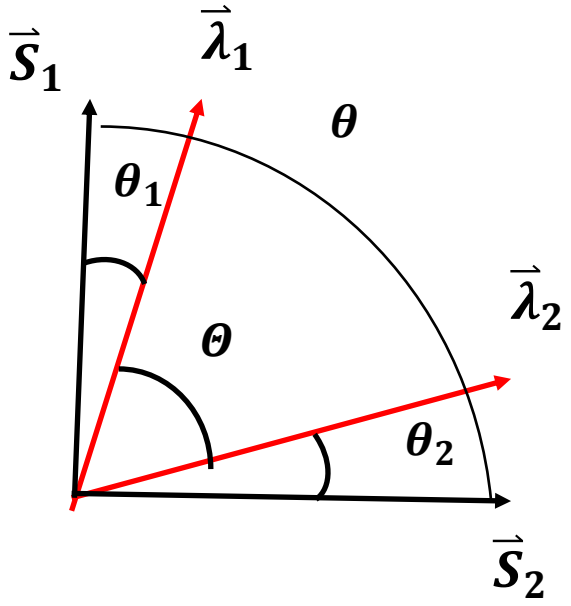
*E. O. Wollan and W. C. Koehler, Phys. Rev. 100, 545 (1955)*

# *Double Exchange: Semiclassical Molecular Field Theory*

## Two-sublattice : Magnetic behavior at finite temperature

$\lambda = |\vec{\lambda}_1| = |\vec{\lambda}_2|$

$$\omega_n(\vec{S}) = \frac{1}{v} e^{-\frac{\vec{\lambda}_n \cdot \vec{S}}{S}}, \; n = 1, 2 \qquad v = \frac{2 sinh\lambda}{\lambda}$$




$$F = -T\mathbb{S} + E_D + E_{ex}$$

$$\mathbb{S} = -k_B N \int_{-1}^{1} \omega_n(x) ln\omega_n(x)\, dx = -k_B N(\lambda m - lnv)$$

***Relative saturation for each sublattice:***

$$m = \frac{1}{v} \int_0^{\pi} d\alpha\, sin\alpha\, cos\alpha\, e^{-\lambda cos\alpha} = -\frac{1}{\lambda} + cotanh\lambda$$

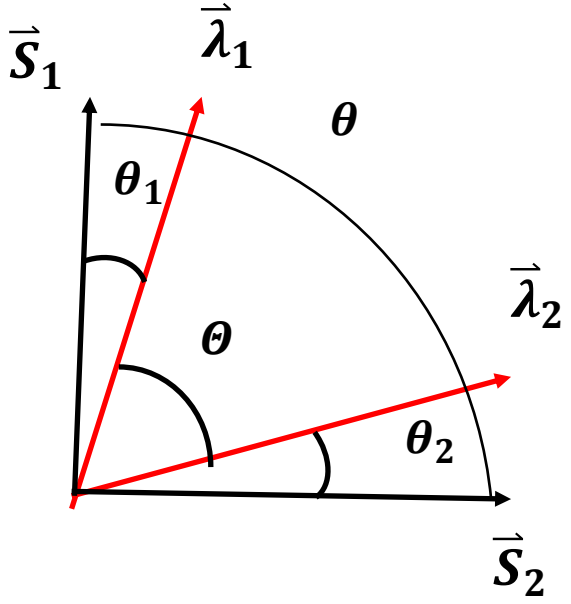
$$E_{ex} = -Nm^2[z'J' + zJ\, cos\, \Theta]$$

# *Double Exchange: Semiclassical Molecular Field Theory*

## Two-sublattice : Magnetic behavior at finite temperature

$$\lambda = |\vec{\lambda}_1| = |\vec{\lambda}_2| \propto \frac{1}{T}$$

$$F = -T\mathbb{S} + E_D + E_{ex}$$




$$\hat{E}_{\vec{k}} = \sum_j^{n.b.} e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_i)} \hat{b}_{ij} = \sum_j^{n.b.} \hat{b}_{ij} \qquad \vec{k}\cdot(\vec{R}_j - \vec{R}_i) \ll 1 \qquad e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_i)} \approx 1$$

**Thermal average for tow sublattice case:**

$$E_D = N \sum_j^{n.b.} -|b_{ij}| \left\langle \cos\frac{\theta_{ij}}{2} \right\rangle = -Nz'b' \left\langle \cos\frac{\theta'}{2} \right\rangle - Nzb \left\langle \cos\frac{\theta}{2} \right\rangle$$

$$\left\langle \cos\frac{\theta}{2} \right\rangle = \frac{-2}{{j_0}^2(-i\lambda)} \sum_{l=0}^{\infty} \frac{{j_l}^2(-i\lambda) P_l(\cos\Theta)}{(2l-1)(2l+3)}; \quad \left\langle \cos\frac{\theta'}{2} \right\rangle = \frac{-2}{{j_0}^2(-i\lambda)} \sum_{l=0}^{\infty} \frac{{j_l}^2(-i\lambda)}{(2l-1)(2l+3)} \qquad \langle A \rangle \equiv \frac{1}{v} \int_0^{\pi} d\alpha \, \sin\alpha \, A \, e^{-\lambda\cos\alpha}$$

$$E_D = \frac{2Nxz}{{j_0}^2(-i\lambda)} \sum_{l=0}^{\infty} \frac{{j_l}^2(-i\lambda) P_l(\cos\Theta)}{(2l-1)(2l+3)} [z'b' + zbP_l(\cos\Theta)]$$

# *Double Exchange: Semiclassical Molecular Field Theory*

## Two-sublattice : Magnetic behavior at finite temperature

$$F = -T\mathbb{S} + E_D + E_{ex} = k_B NT(\lambda m - lnv) + \frac{2Nxz}{j_0{}^2(-i\lambda)} \sum_{l=0}^{\infty} \frac{j_l{}^2(-i\lambda)P_l(cos\Theta)}{(2l-1)(2l+3)} [z'b' + zbP_l(cos\Theta)]$$

$$-Nm^2[z'J' + zJ\,cos\,\Theta]$$

$$\frac{\delta F}{\delta u} = 0, \qquad m^2 + \frac{\xi}{j_0{}^2(-i\lambda)} \sum_{l=0}^{\infty} \frac{j_l{}^2(-i\lambda)}{(2l-1)(2l+3)} \frac{dP_l(cos\Theta)}{dv} = 0 \qquad u = cos\,\Theta \qquad \xi = \frac{bx}{|J|S^2}$$

*(1) Low temperature:* $\lambda \propto \frac{1}{T} \to \infty$ $\qquad -1 < u = cos\,\Theta < 1$ $\qquad$ *Canted spin arrangement*

*(2) High temperature:* $\lambda \propto \frac{1}{T} \to 0$ $\qquad$ $\mathrm{u} > 1$: ferromagnetic ; $\mathrm{u} < -1$: antiferromagnetic ;

$$\mathrm{u} = 1, \frac{1}{\xi} = \frac{-1}{j_0{}^2(-i\lambda)m^2} \sum_{l=0}^{\infty} \frac{j_l{}^2(-i\lambda)\, l(l+1)}{(2l-1)(2l+3)} \qquad \mathrm{u} = -1, \frac{1}{\xi} = \frac{-1}{j_0{}^2(-i\lambda)m^2} \sum_{l=0}^{\infty} \frac{j_l{}^2(-i\lambda)(-1)^{l+1}\, l(l+1)}{(2l-1)(2l+3)}$$

# *Double Exchange: Semiclassical Molecular Field Theory*

## Two-sublattice : Magnetic behavior at finite temperature

If $\mathbf{u} > 1, \mathbf{u} < -1$

$$F = F_0 + F_2 m^2 + F_4 m^4 + \cdots,$$

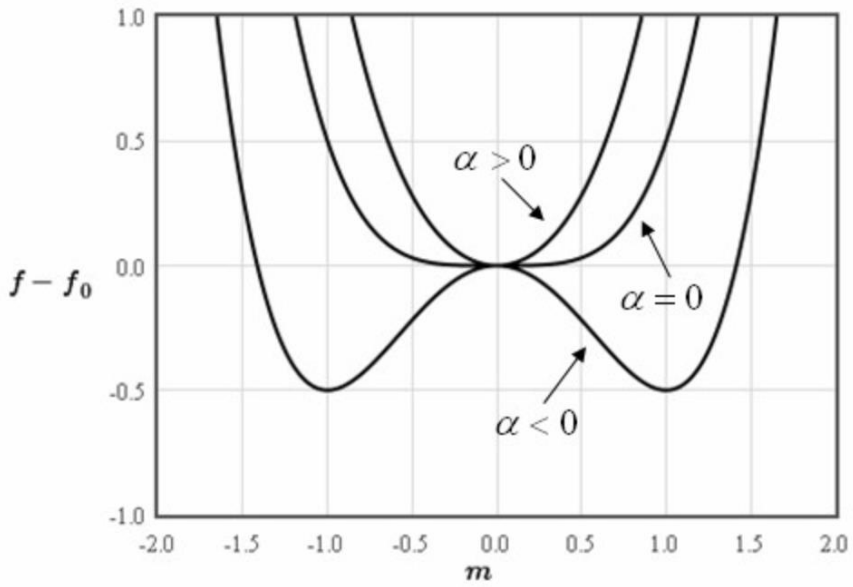
$$F_2 = N\left[\frac{3}{2}k_B T - S^2(z'J' + zJu) - \frac{2x}{5}((z'b' + zbu))\right] \quad F_4 = N\left[\frac{9}{20}k_B T + \frac{6x}{7}((z'b' + zbu))\right], \mathbf{u} = \pm 1$$

$F$ minimized when $m^2 = -\frac{F_2}{2F_4}, \quad F_2 < 0$

$F_2 = 0$ ➡

$$T_C = \frac{3}{2}k_B\left[S^2(z'J' + zJ) + \frac{2x}{5}((z'b' + zb))\right]$$

$$T_N = \frac{3}{2}k_B\left[S^2(z'J' - zJ) + \frac{2x}{5}((z'b' - zb))\right]$$




$$f(T) = f_0(T) + \alpha_0(T - T_c)m^2 + \frac{1}{2}\beta m^4 \qquad \alpha_0 > 0, \qquad \beta > 0.$$

# *Double Exchange: Semiclassical Molecular Field Theory*

## Two-sublattice : Magnetic behavior at finite temperature

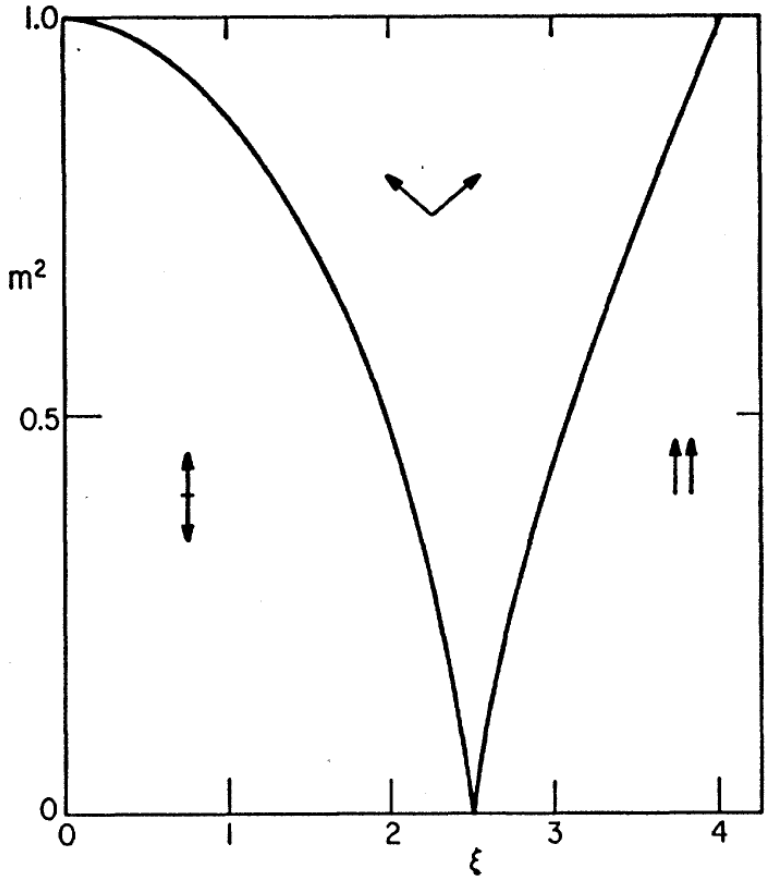
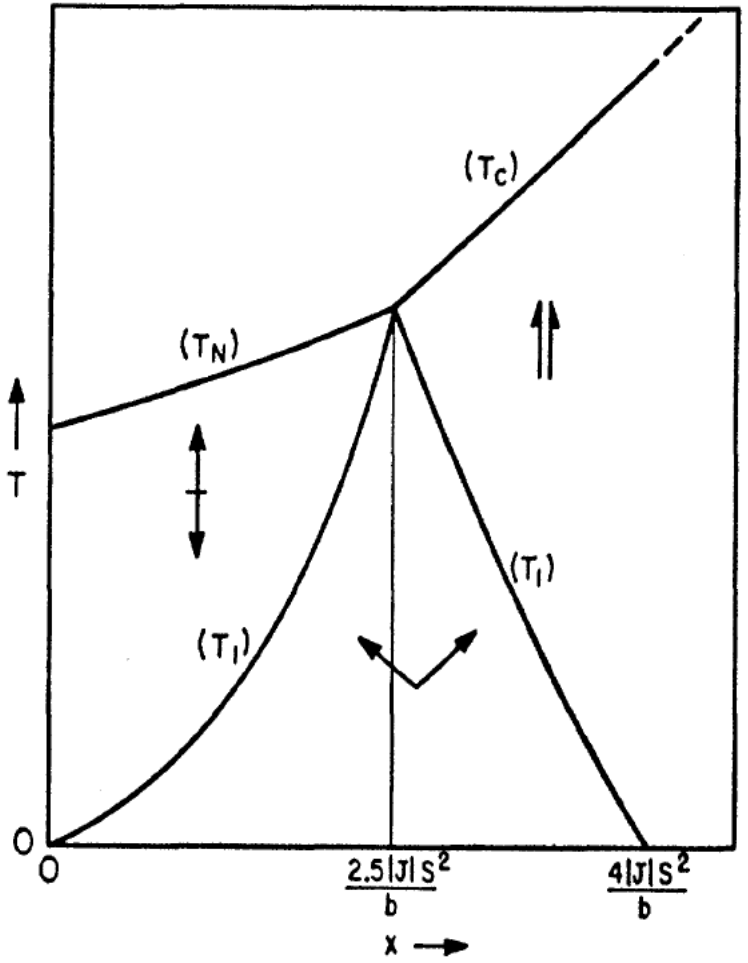



FIG. 4. Square of the relative saturation $m_{T1}=M_{T1}/M_0$ of each sublattice at the lower transition point $T_1$, as a function of $\xi=bx/|J|S^2$.

FIG. 5. Typical "magnetic phase diagram" for a layer antiferromagnet. Theoretical values of $T_1$, $T_c$, and $T_N$ are given in the text.



# Supplementary

# Bloch Theorem: Symmetry + QM

**0. Define the Abelian translation group $\{\hat{T}_{\vec{R}} | \vec{R} = n_i\vec{a}_i, n_i \in Z\}$, where $\{\vec{a}_i\}$ is a Bravais lattice**

**In $\vec{r}$ representation, for any state $\psi(\vec{r})$, $\hat{T}_{\vec{R}}\psi(\vec{r}) = \psi(\vec{r} + \vec{R})$.**

**1. $\hat{T}_{\vec{R}}$ translation symmetry: $[\hat{H}, \hat{T}_{\vec{R}}] = 0$**

**1.1 $\hat{H}\,\psi_{\varepsilon,\vec{k}}(\vec{r}) = \varepsilon\psi_{\varepsilon,\vec{k}}(\vec{r})$; $\hat{T}_{\vec{R}}\psi_{\varepsilon,\vec{k}}(\vec{r}) = \psi_{\varepsilon,\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{\varepsilon,\vec{k}}(\vec{r})$; $\vec{k} = x_i\vec{b}_i$, $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$[1]**

**1.2 Common eigenstates $\psi_{\varepsilon,\vec{k}}(\vec{r})$ as a complete basis**

**1.3 Bragg's law:**

$$\psi_1 = \left(\psi_{\varepsilon,\vec{k}}(\vec{r}) + \psi_{\varepsilon,\vec{k}'}(\vec{r})\right)$$

**1.3.1 $\hat{T}_{\vec{R}}\psi_1$ and $\psi_1$ correspond to the same physical state**

**1.3.2 For any allowed $\vec{R}$, $\vec{k}$ and $\vec{k}'$, $\hat{T}_{\vec{R}}\psi_1 = \hat{T}_{\vec{R}}\psi_{\varepsilon,\vec{k}}(\vec{r}) + \hat{T}_{\vec{R}}\psi_{\varepsilon,\vec{k}'}(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}\psi_{\varepsilon,\vec{k}}(\vec{r}) + e^{i\vec{k}'\cdot\vec{R}}\psi_{\varepsilon,\vec{k}'}(\vec{r}) =$**

$$e^{i\vec{k}\cdot\vec{R}}\left(\psi_{\varepsilon,\vec{k}}(\vec{r}) + e^{i(\vec{k}'-\vec{k})\cdot\vec{R}}\psi_{\varepsilon,\vec{k}'}(\vec{r})\right)$$

$\Rightarrow$ $e^{i(\vec{k}'-\vec{k})\cdot\vec{R}} = 1$ **or** $(\vec{k}' - \vec{k})\cdot\vec{R} = 2\pi n, n \in Z$ **or** $\vec{k}' - \vec{k} = \vec{G} = m_i\vec{b}_i, m_i \in Z$

**2. Energy level and state wavefunction[2]**

$$\psi(\vec{r}) = \sum_{\vec{k}} C(\vec{k})e^{i\vec{k}\cdot\vec{r}} \qquad V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}$$

**2.1 $\psi_{\varepsilon,\vec{k}}(\vec{r}) = u_{\varepsilon,\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$, $u_{\varepsilon,\vec{k}}(\vec{r}) \equiv \sum_{\vec{G}} C(\vec{k} - \vec{G})\, e^{-i\vec{G}\cdot\vec{r}}$**

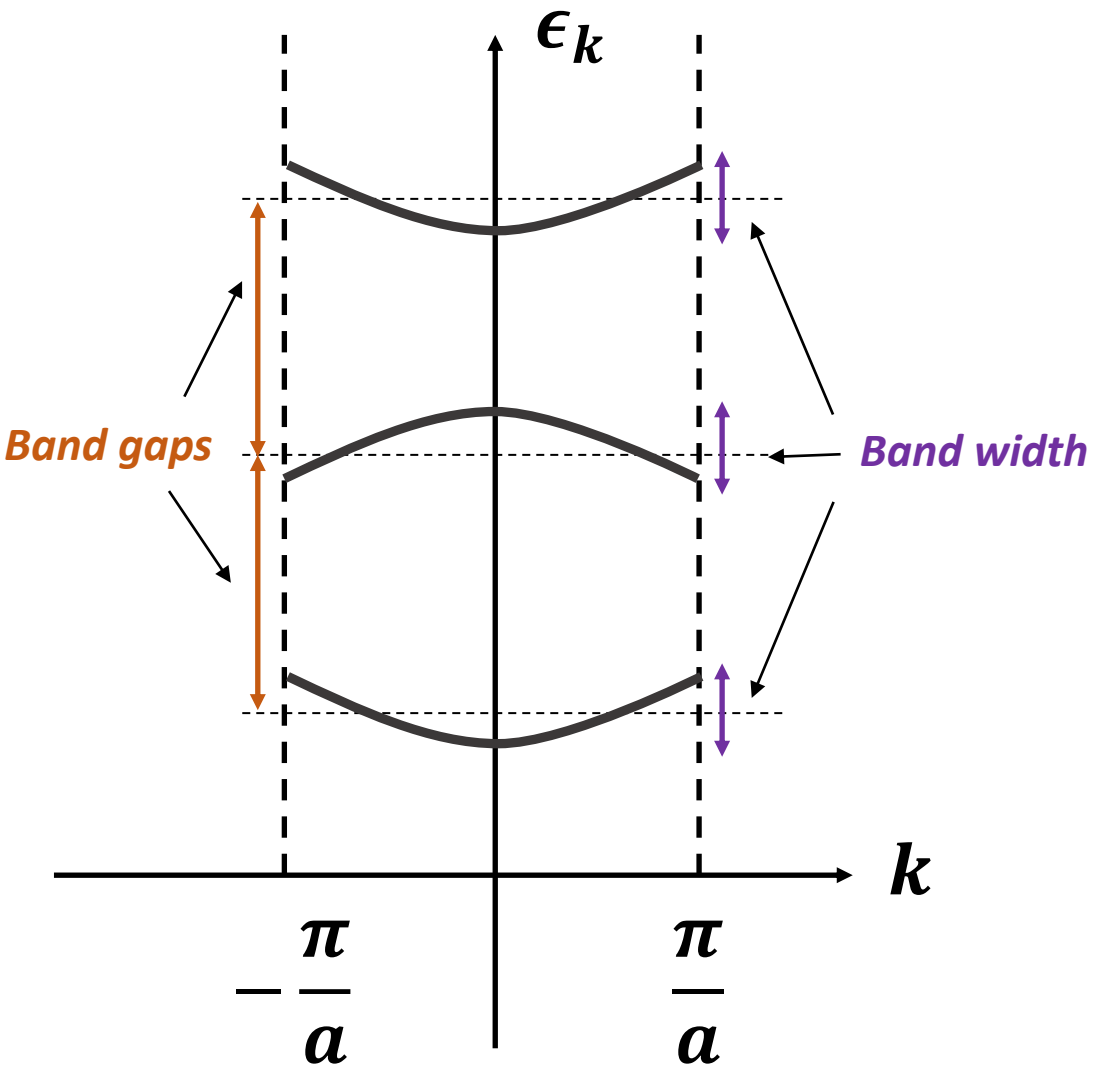
**2.2 All info included in the 1st Brillouin zone**

$$\varepsilon(\vec{k}) = \varepsilon(\vec{k} + \vec{G})$$

*Schrodinger equation:* $\left(\frac{\hbar^2 k^2}{2m} - \varepsilon\right) C(\vec{k}) + \sum_{\vec{G}} C(\vec{k} - \vec{G})\, V_{\vec{G}} = 0$

# Tight-binding Model[3]: large interatomic distance limitation

## Narrow bands separated by large gaps




## 1. Band Theory

## 2. Eigenfunction as a linear combination of atomic orbitals

### 2.1) single atomic orbital case

$$\psi_{m,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N(1+\sum_{\vec{R}_l\neq 0} e^{i\vec{k}\cdot\vec{R}_l}\alpha_{m,m}(\vec{R}_l))}}\sum_j^N e^{i\vec{k}\cdot\vec{R}_j}\varphi_m(\vec{r}-\vec{R}_j);$$

Atomic overlap integrals of the same orbital m from different atoms $\alpha_{m,m}(\vec{R}_l) \equiv \int d^3r\varphi_m(\vec{r})^*\varphi_m(\vec{r}-\vec{R}_j) \ll 1$

### 2.2) Hybridization case

$$\psi_{m,\vec{k}}(\vec{r}) = \sum_n^\infty a_{mn,\vec{k}}\frac{1}{\sqrt{N}}\sum_j^N e^{i\vec{k}\cdot\vec{R}_j}\varphi_n(\vec{r}-\vec{R}_j)$$

where the sum over a complete set of atomic orbitals, including continuum scattering states; $a_{mn,\vec{k}}$ *describes the mixing of m-th and n-th bands, and could be solved by diagonalizing the Hamiltonian*.

## 3. $H = \sum_j^N H_{at}(\vec{r}-\vec{R}_j) + \Delta U(\vec{r})$

$$H_{at}(\vec{r}-\vec{R}_j) \equiv \frac{{p_j}^2}{2m_j} + v(\vec{r}-\vec{R}_j)$$

$$\varepsilon_{m,\vec{k}} = E_m + \frac{\beta_{m,m} + \sum_{\vec{R}_l\neq 0} e^{i\vec{k}\cdot\vec{R}_l}\gamma_{m,m}(\vec{R}_l)}{N(1+\sum_{\vec{R}_l\neq 0} e^{i\vec{k}\cdot\vec{R}_l}\alpha_{m,m}(\vec{R}_l))}$$

$$\beta_{m,m} \equiv \int d^3r{\varphi_m}^*(\vec{r})\Delta V(\vec{r})\varphi_m(\vec{r}) \qquad \gamma_{m,m}(\vec{R}_l) \equiv \int d^3r{\varphi_m}^*(\vec{r}-\vec{R}_l)\Delta V(\vec{r})\varphi_m(\vec{r})$$

$$\Delta V(\vec{r}) \equiv \sum_{\vec{R}_l\neq 0} v(\vec{r}-\vec{R}_l) + \sum_{\vec{R}_l}\Delta U(\vec{r}+\vec{R}_l)$$

# *Tight-binding Model: Energy for Double Exchange*

$$\psi_{3d,\vec{k}} = \frac{1}{\sqrt{N}} \sum_{j}^{N} e^{i\vec{k}\cdot\vec{R}_j} |\vec{R}_j\rangle$$

$$\Delta H |\psi_{3d,\vec{k}}\rangle = E_{\vec{k}} |\psi_{3d,\vec{k}}\rangle \quad \Rightarrow \quad \langle \vec{R}_i | \Delta H | \psi_{3d,\vec{k}} \rangle = E_{\vec{k}} \langle \vec{R}_i | \psi_{3d,\vec{k}} \rangle$$

$$\langle R_i | \Delta H | R_j \rangle = \hat{b}_{ij}$$

$$l.h.s = \langle \vec{R}_i | \Delta H | \psi_{3d,\vec{k}} \rangle = \frac{1}{\sqrt{N}} \sum_{j}^{N} e^{i\vec{k}\cdot\vec{R}_j} \langle \vec{R}_i | \Delta H | \vec{R}_j \rangle = \frac{1}{\sqrt{N}} \sum_{j}^{n.b.} e^{i\vec{k}\cdot\vec{R}_j} \hat{b}_{ij}$$

$$r.h.s = E_{\vec{k}} \langle \vec{R}_i | \psi_{3d,\vec{k}} \rangle = \frac{1}{\sqrt{N}} E_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_i}$$

$$l.h.s = r.h.s \quad \Rightarrow \quad E_{\vec{k}} = \sum_{j}^{n.b.} e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_i)} \hat{b}_{ij}$$

$n.b. \equiv$ ***nearest neighbors of site i, including i***

# ***Wannier Function:*** *from Bloch states to local orbitals*

***Periodicity of crystal lattice:*** $$\psi_{m,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{j=1}^{N} a_m(R_j,\vec{r})e^{i\vec{k}\cdot\vec{R}_j}$$

***Localized orbitals as Wannier function:*** $$a_m(R_j,\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}} \psi_{m,\vec{k}}(\vec{r})e^{-i\vec{k}\cdot\vec{R}_j}$$

**1.** $a_m(R_j,\vec{r}) = a_m(\vec{r}-R_j)$**, i.e.** $\forall$ **lattice vector** $R_n$, $a_m(R_j,\vec{r}) = a_m(R_j+R_n,\vec{r}+R_n)$

$Hint$: $\psi_{\varepsilon,\vec{k}}(\vec{r}+R_n) = e^{i\vec{k}\cdot R_n}\psi_{\varepsilon,\vec{k}}(\vec{r})$;

**2. An orthonormal basis:** $$\int d^3r\, a_m{}^*(R_k,\vec{r})a_m(R_j,\vec{r}) = \delta_{R_k,R_j}$$

**3. Since Bloch states defined up to an overall phase** $\psi_{m,\vec{k}}(\vec{r}) \to e^{i\theta}\psi_{m,\vec{k}}(\vec{r})$**, Wannier function can be chosen as the maximally-localized set:** $a_m(R_j,\vec{r})$ **localized around** $R_j$ **and rapidly goes to zero away from** $R_j$**. For 1-dimension and separable potential cases in higher dimensions, the maximally-localized set is unique.**[4]

# References

[1] https://www.tf.uni-kiel.de/matwis/amat/q_mech/kap_1/backbone/r_se24.html
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[3] https://www.cond-mat.de/events/correl12/manuscripts/pavarini.pdf
[4]W. Kohn (1959). "Analytic Properties of Bloch Waves and Wannier Functions". Physical Review. **115** (4): 809–821.