

For octahedral			high spin							
e	g ——			+	<u>+</u> ‡	<u>+</u> ‡	++	++	∔ ‡	<u>t</u> tt
t	22		<u>†††</u>	↓ ↓↓	ŧ †Ť	ŧ ţ‡‡	ŧţţţÎ	tutil	ţţţ	<u>†ţ†ţŤI</u>
	d ¹	d ²	d ³	d ⁴	d ⁵	d ⁶	d ⁷	d ⁸	d9	d ¹⁰
S =	1/2	1	3/2	2	5/2	2	3/2	1	1/2	0
	Ti ³⁺	Ti ²⁺	Cr^{3+}	Cr ²⁺	Fe ³⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu^{2+}	Zn^{2+}
	V ⁴⁺	V ³⁺	Mn ⁴⁺	Mn ³⁺	Mn ²⁺	Co ³⁺	Ni ³⁺			Cu ⁺
				Ti ⁰	\mathbf{V}^0	Cr ⁰	Mn^0	Fe ⁰	\mathbf{Co}^0	Ni ⁰
				4	5	6	7	8	9	10
Fo	or $d = 4$	∽7, wh	en cryst	al field :	> Hund	rule, lo	ow spin	state ad	chieved	
Trans	sition fro	om higł	ı spin				+	[F	e ^{II} (phei	$n)_2(NCS)_2]$
to lov	w spin b	y chang	ging T		. +1		. Auto	χī	r^{\uparrow} 1	76 K
Spin	crossov	er		₽ ₽₽	¶‡I¥	1111	îţi‡++	λ -	low	· · · · · · · · · · · · · · · · · · ·
Low spin d ⁶ is			d^4	d ⁵	d ⁶	d ⁷		spin	high spir	
non	magnet	ic	C -	- 1	1/2	0	1/2		r)







Magnetic Order	<u>†</u> †
Ferromagnetism: all parallel	$\uparrow \qquad J > 0$ $\uparrow \qquad f \qquad S_i / / S_j \text{ is stable}$
Antiferromagnetism: alternately opposite directions	$\downarrow \uparrow \qquad J < 0$ $\uparrow \downarrow \qquad \text{Antiparallel } S_i \text{ and } S_j$
Spin Hamiltoniam $\hat{H} = -\sum_{i, j} 2J_{ij} \overline{S}_i \overline{S}_j - g\mu_{\rm B} H \sum_i \overline{S}_i$ Interaction Zeemann splitting	$ \begin{array}{c} \downarrow \uparrow \\ S_z \\ h/2 \\ a \\ S_x \\ S_y \\ -h/2 \\ \beta \end{array} $
S_i is a vector like (S_x, S_y, S_z) : (Heisenberg when spin is always directed in one direction anisotropy coming from the crystal field (Is	model). Exction (z) due to the large magnetic , we only consider S_z . sing model)
When $S_i = 1/2$, $S_j = 1/2$, (Interaction) = -J When $S_i = 1/2$, $S_j = -1/2$, (Interaction) = -J	I/2 Energy difference J
Note: (Interaction) is defined as $-\sum J_{ij}\overline{S}_i\overline{S}_i$	S_j in old literatures.
i,j	J is twice larger.







Low dimensional fluctuation	
ID Magnet does not exist (Landau, Lifshitz Statistical Physics) Statistical weight of a state with <i>n</i> boundaries in a 1D	L原子
ferromagnet (length L): $W = \frac{L!}{L!}$	
$\ln W = L \ln L - (L - n) \ln (L - n) - n \ln n$	n界面
$= L \ln \frac{L}{L-n} + n \ln \frac{L-n}{n} \approx -n \ln \frac{n}{L} \qquad n \ll L \to \Re 1 \mathfrak{T}$	∽0
The free energy is $G = G_0 - TS + nJ = G_0 + k_B Tn \ln \frac{n}{L} + n$	J
Realized <i>n</i> is obtained by minimizing <i>G</i> : $\frac{\partial G}{\partial n} = k_{\rm B}T \ln \frac{n}{L} + J (=0)$	<i>T</i> c
$\ln(n/L)$ takes a large negative value for small n/L , so near $n \sim 0$	$: \frac{\partial \theta}{\partial x} < 0$
With increasing <i>n</i> , <i>G</i> decreases.	On
Accordingly, there is a minimum of G at finite $n \neq 0$.	
For finite $T \neq 0$, many boundaries appear, and long-range magnet	etic order
is never established. Then there is no 1D ferromagnet.	
Multi dimension increases the loss of <i>J</i> , and leads to long range a	nagnetic order.
In general, a 1D system does not undergo any phase transitions	at finite <i>T</i> .







2次元三角格子, N. Elstner, et al. *Phys. Rev. Lett.* **71**, 1629 (1993); M. Tamura and R. Kato, *J. Phys. Cond. Matter.* **14**, L729 (2002). 1次元フェリ, R. Georges et al. *Magnetism: Molecules to Materials*, ed. by J. S. Miller and M. Drillon, Wiley (2001), p1.









J(交換相互作用)= <u>K</u> (交換積分)		1 - E	_	二里垻
(1) Degenerated 2 levels (e.g. on the	e same mol.)	1	2	+ +
Triplet is more stable by:			<i>I</i> ₁₂	$J_{12} - K_{12}$
$K_{12} = \int \varphi_1^*(1)\varphi_2^*(2)\frac{e^2}{r}\varphi_1(2)\varphi_2(1)d$	$\tau > 0$ (potential)	tial exchan	ge)。	
→spin parallel (強磁性的) (Hu	nd規則)←交	を換積分		
(2) Nearby 2 atoms	(a) <u></u> t	(b)	U	(c) X
Electron moves from 原子1 to 原子2 by transfer積分t. Energy increases by the on-site C Mixing the (b) state, and the (a) s Parallel spin (c) is not stabilized	1 2 Coulomb積分 state is stabili due to the Pa	U (b) . Go ized by uli exclusi	the back on prince	tek to (a) $J = -\frac{2t^2}{U}$ ciple,
So antiparallel (a) is more stable Usually (2)>>(1) leads to 反強磁	by J (kinetic 结件.J<0 domi	exchange) nant.	•	
	.2		O.	
Lamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-1]$	$-\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}\right)$	$-)] + \frac{1}{4\pi a}$	$\frac{1}{\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$
Lamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-1]$ Calculate $E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$	$\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$	$\frac{\varepsilon_0}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}\right)$	$-)] + \frac{1}{4\pi a}$	$rac{1}{r_{0}} (rac{1}{r_{12}} + rac{1}{r_{AB}})$
Tamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$	$-\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}\right)$	$(-)] + \frac{1}{4\pi a}$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$
Iamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J+K}{1+S^{2}}$	$-\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}\right)$	$(-)] + \frac{1}{4\pi a}$	$rac{1}{r_{0}} (rac{1}{r_{12}} + rac{1}{r_{AB}})$
Iamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J+K}{1+S^{2}}$ α : one-electron energy of a hydrog	$-\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}\right)$ from the nucleus	$-)] + \frac{1}{4\pi a}$	$\overline{c_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}}\right)$
Iamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J+K}{1+S^{2}}$ α : one-electron energy of a hydrog $J = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\epsilon} [\frac{1}{r} + \frac{1}{2}]$	$\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom $\frac{1}{r} - \frac{1}{r}$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}} \right)$ from mucleus $\frac{1}{r_i} \chi_A(1)$	$-)] + \frac{1}{4\pi a}$ C $\chi_{\rm B}(2)d$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$ Coulomb integrating $\tau_1 d \tau_2 < 0$
Iamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J + K}{1 + S^{2}}$ α : one-electron energy of a hydrog $J = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K_{12}]$	$\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom $\frac{1}{r_{AB}} - \frac{1}{r_{A2}}$ 1	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}} \right)$ from mucleus $\frac{1}{r_{B1}} \chi_A(1)$ $\frac{1}{r_{B1}} \chi_A(1)$	$\frac{1}{2} + \frac{1}{4\pi u}$ $\frac{1}{2}$ \frac	$\frac{1}{r_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$ Coulomb integral $\tau_1 d \tau_2 < 0$ Exchange integral $\tau_2 d \tau_2 = 0$
Hamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J+K}{1+S^{2}}$ α : one-electron energy of a hydrog $J = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K = \frac{1}{2} \int \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K + K + K + K + K + K + K + K + K +$	$\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom $\frac{1}{r_{AB}} - \frac{1}{r_{A2}} - \frac{1}{r_{A2}}$	$\frac{1}{\varepsilon_0} \frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}$ from nucleus $\frac{1}{r_{B1}} \chi_A(1)$ $\frac{1}{r_{B1}} \chi_A(2)$	$\frac{1}{4\pi a}$ 1	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$ Coulomb integrate $\tau_1 d \tau_2 < 0$ Exchange integrate $\tau_1 d \tau_2 < 0$
Iamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J + K}{1 + S^{2}}$ α : one-electron energy of a hydrog $J = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K = \frac{1}{2} \int \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K + \frac{1}{2} \int \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} \frac{1}{r_{12}} + \frac{1}{2} \int \chi_{A}(1)\chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} \frac{1}{r_{12}} + \frac{1}{2} \int \chi_{A}(1)\chi_{A}(1$	$\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom $\frac{1}{r_{AB}} - \frac{1}{r_{A2}}$ $+ \frac{1}{r_{AB}} - \frac{1}{r_{A2}} - \frac{1}{r_{A2}}$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}} \right)$ from mucleus $\frac{1}{r_{B1}} \chi_A(1)$ $\frac{1}{r_{B1}} \chi_A(2)$ O	$\frac{1}{2} + \frac{1}{4\pi u}$ $\frac{1}{4\pi u}$ $\frac{1}{2}$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$ Coulomb integrating $\tau_1 d \tau_2 < 0$ Exchange integrate $\tau_1 d \tau_2 < 0$ order
Hamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J+K}{1+S^{2}}$ α : one-electron energy of a hydrog $J = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K + K + K + K + K + K + K + K + K +$	$\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom $\frac{1}{r_{AB}} - \frac{1}{r_{A2}} - \frac{1}{r_{A2}}$ $+ \frac{1}{r_{AB}} - \frac{1}{r_{A2}} - \frac{1}{r_{A3}} - 1$	$\frac{1}{\varepsilon_0} \frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}$ from nucleus $\frac{1}{r_{B1}} \chi_A(1)$ $-\frac{1}{r_{B1}} \chi_A(2)$ ls in MO (2)	$\frac{1}{4\pi a}$ 1	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$ Coulomb integrate $\tau_1 d \tau_2 < 0$ Exchange integrate $\tau_1 d \tau_2 < 0$ order
Hamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J+K}{1+S^{2}}$ α : one-electron energy of a hydrog $J = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K]$ $K = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K]$ Different from Coulomb and exch The above contain nuclear attraction This is the origin of the covalent b	$\frac{h^2}{2m} \nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom $\frac{1}{r_{AB}} - \frac{1}{r_{A2}}$ $+ \frac{1}{r_{AB}} - \frac{1}{r_{A2}}$ ange integration, and <0, bond.	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}} \right)$ from mucleus $\frac{1}{r_{B1}} \chi_A(1)$ $-\frac{1}{r_{B1}} \chi_A(2)$ Is in MO (2)	$(1)^{2} + \frac{1}{4\pi a}$ $(2)^{2} + \frac{1}{4\pi a}$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$ Coulomb integence i
Hamiltonian of hydrogen mol. $H = \sum_{i=1,2} [-Calculate E = \int \Psi H \Psi d\tau / \int \Psi \Psi d\tau$ $E_{+} = 2\alpha + \frac{J + K}{1 + S^{2}}$ α : one-electron energy of a hydrog $J = \iint \chi_{A}(1)\chi_{B}(2) \frac{1}{4\pi\varepsilon_{0}} [\frac{1}{r_{12}} + K = \lim_{k \to \infty} [\frac{1}{2} + \frac{1}{2} + \frac{1}{2$	$\frac{h^2}{2m}\nabla_i^2 - \frac{1}{4\pi}$ Repulsion the nearby gen atom $\frac{1}{r_{AB}} - \frac{1}{r_{A2}}$ $+ \frac{1}{r_{AB}} - \frac{1}{r_{A2}}$ hange integration, and <0.	$\frac{1}{\varepsilon_0} \frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}$ from nucleus $\frac{1}{r_{Bi}} \chi_A(1)$ $-\frac{1}{r_{Bi}} \chi_A(2)$ Is in MO (2)	$\frac{1}{2} = \frac{1}{4\pi a}$ $\frac{1}{4\pi a}$ $\frac{1}{4$	$\frac{1}{\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$ Coulomb integrates $\tau_1 d \tau_2 < 0$ exchange integrates $\tau_1 d \tau_2 < 0$ order E

 $E_{-} = 2\alpha + \frac{J - K}{1 - S^2}$













Expe	erimentally distir	iguish origins of	metal-insulator	transitions
	電気抵抗率	静磁化率 (SQUID)	スピン磁化率 (ESR)	X線散乱
電荷密度 波(CDW) (Peierls 転移)	 	<i>X</i> ∗ 非磁性絶縁体	X _s the same 連続線幅 at $T_{\rm MI}$ $\chi \propto \frac{1}{k_{\rm B}T (3 + e^{E_{\rm g}/k_{\rm B}T})}$	$2k_{\rm F}$ 長周期 > $T_{\rm MI}$ 散漫散乱 < $T_{\rm MI}$ spots
Spin 密度波 (SDW)	ρ _ 絶縁体 金属 	反強磁性絶縁体 X X J X J T _{MI} T	↓線幅発散 → 強度 → T	non →0
Mott 絶縁体・ 電荷整列	^ρ		The same χ_s 線幅連続 at T_{MI} SDW or spin-Peierls at lower T	Mott:non 電荷整列: 長周期
Spin- Peierls 転移		X → 非磁性絶縁体	The same <i>χ</i> s 線幅連続 at <i>T</i> _{MI} The same as CDW singlet-triplet mode	2k _F の長周期 el



