

# 物性化学 II

大学院理学研究科 化学専攻

北川 宏

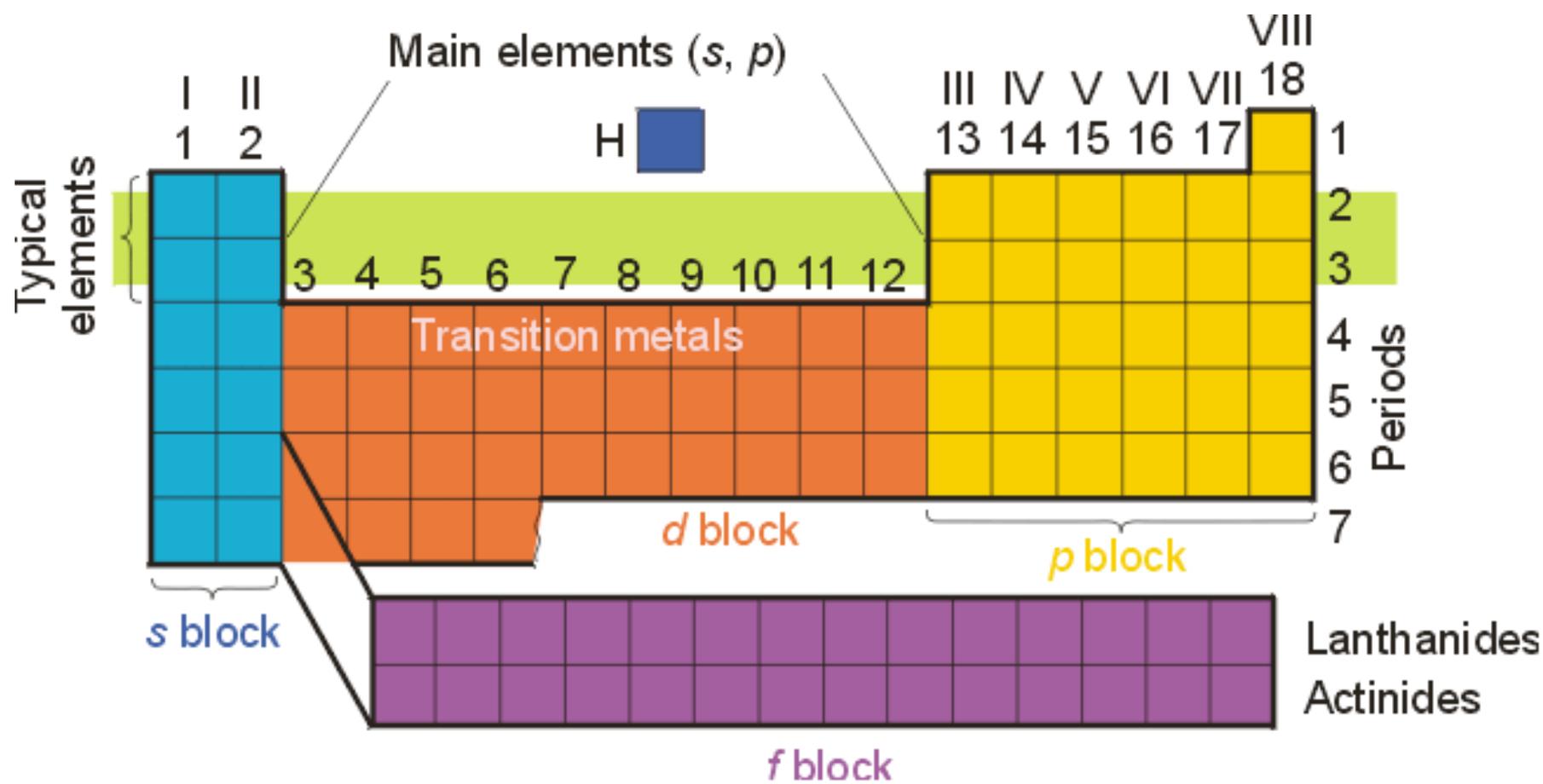
木曜日 5限目

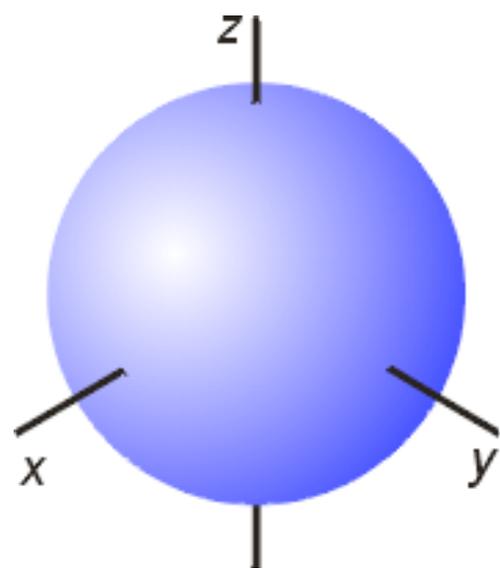
# IUPAC Periodic Table of the Elements

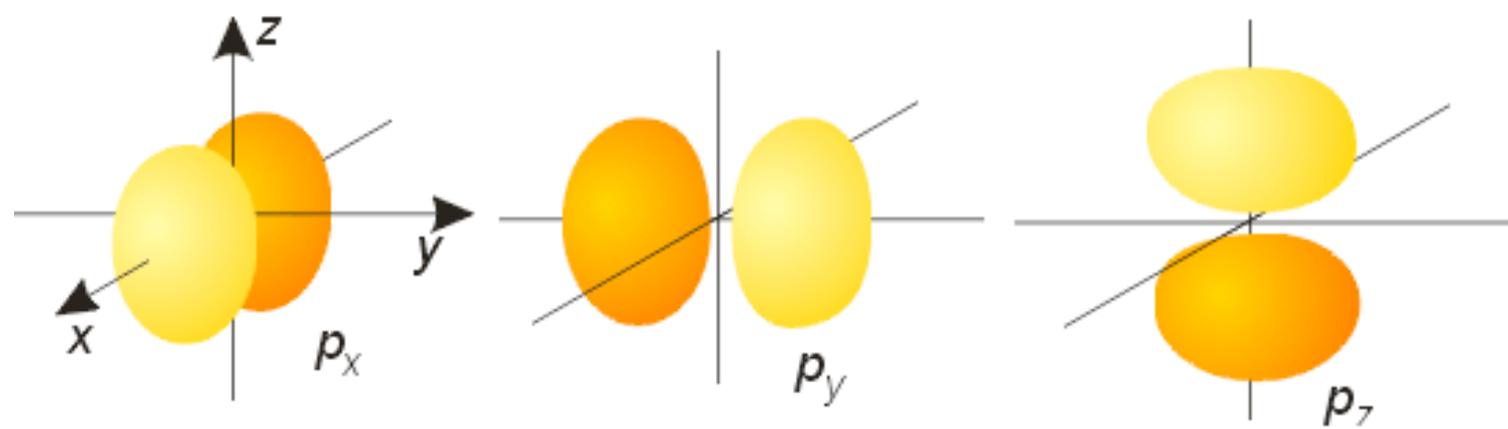
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 <b>H</b> hydrogen 1.007 94(7)																	2 <b>He</b> helium 4.002 602(2)
3 <b>Li</b> lithium 6.941(2)	4 <b>Be</b> beryllium 9.012 182(3)											5 <b>B</b> boron 10.811(7)	6 <b>C</b> carbon 12.0107(8)	7 <b>N</b> nitrogen 14.0067(2)	8 <b>O</b> oxygen 15.9994(3)	9 <b>F</b> fluorine 18.998 4032(5)	10 <b>Ne</b> neon 20.1797(6)
11 <b>Na</b> sodium 22.989 770(2)	12 <b>Mg</b> magnesium 24.3050(6)											13 <b>Al</b> aluminium 26.981 538(2)	14 <b>Si</b> silicon 28.0855(3)	15 <b>P</b> phosphorus 30.973 761(2)	16 <b>S</b> sulfur 32.065(5)	17 <b>Cl</b> chlorine 35.453(2)	18 <b>Ar</b> argon 39.948(1)
19 <b>K</b> potassium 39.0983(1)	20 <b>Ca</b> calcium 40.078(4)	21 <b>Sc</b> scandium 44.955 910(8)	22 <b>Ti</b> titanium 47.867(1)	23 <b>V</b> vanadium 50.9415(1)	24 <b>Cr</b> chromium 51.9961(6)	25 <b>Mn</b> manganese 54.938 049(9)	26 <b>Fe</b> iron 55.845(2)	27 <b>Co</b> cobalt 58.933 200(9)	28 <b>Ni</b> nickel 58.6934(2)	29 <b>Cu</b> copper 63.546(3)	30 <b>Zn</b> zinc 65.409(4)	31 <b>Ga</b> gallium 69.723(1)	32 <b>Ge</b> germanium 72.64(1)	33 <b>As</b> arsenic 74.921 60(2)	34 <b>Se</b> selenium 78.96(3)	35 <b>Br</b> bromine 79.904(1)	36 <b>Kr</b> krypton 83.798(2)
37 <b>Rb</b> rubidium 85.4678(3)	38 <b>Sr</b> strontium 87.62(1)	39 <b>Y</b> yttrium 88.905 85(2)	40 <b>Zr</b> zirconium 91.224(2)	41 <b>Nb</b> niobium 92.906 38(2)	42 <b>Mo</b> molybdenum 95.94(2)	43 <b>Tc</b> technetium [97.9072]	44 <b>Ru</b> ruthenium 101.07(2)	45 <b>Rh</b> rhodium 102.905 50(2)	46 <b>Pd</b> palladium 106.42(1)	47 <b>Ag</b> silver 107.8682(2)	48 <b>Cd</b> cadmium 112.411(8)	49 <b>In</b> indium 114.818(3)	50 <b>Sn</b> tin 118.710(7)	51 <b>Sb</b> antimony 121.760(1)	52 <b>Te</b> tellurium 127.60(3)	53 <b>I</b> iodine 126.904 47(3)	54 <b>Xe</b> xenon 131.293(6)
55 <b>Cs</b> caesium 132.905 45(2)	56 <b>Ba</b> barium 137.327(7)	57-71 lanthanoids	72 <b>Hf</b> hafnium 178.49(2)	73 <b>Ta</b> tantalum 180.9479(1)	74 <b>W</b> tungsten 183.84(1)	75 <b>Re</b> rhenium 186.207(1)	76 <b>Os</b> osmium 190.23(3)	77 <b>Ir</b> iridium 192.217(3)	78 <b>Pt</b> platinum 195.078(2)	79 <b>Au</b> gold 196.966 55(2)	80 <b>Hg</b> mercury 200.59(2)	81 <b>Tl</b> thallium 204.3833(2)	82 <b>Pb</b> lead 207.2(1)	83 <b>Bi</b> bismuth 208.980 38(2)	84 <b>Po</b> polonium [208.9824]	85 <b>At</b> astatine [209.9871]	86 <b>Rn</b> radon [222.0176]
87 <b>Fr</b> francium [223.0197]	88 <b>Ra</b> radium [226.0254]	89-103 actinoids	104 <b>Rf</b> rutherfordium [261.1088]	105 <b>Db</b> dubnium [262.1141]	106 <b>Sg</b> seaborgium [266.1219]	107 <b>Bh</b> bohrium [264.12]	108 <b>Hs</b> hassium [277]	109 <b>Mt</b> meitnerium [268.1388]	110 <b>Ds</b> darmstadtium [269]	111 <b>Uuu</b> unununium [272]	112 <b>Uub</b> ununbium [285]		114 <b>Uuq</b> ununquadium [289]		116 <b>Uuh</b> ununhexium [289]		
			57 <b>La</b> lanthanum 138.9055(2)	58 <b>Ce</b> cerium 140.116(1)	59 <b>Pr</b> praseodymium 140.907 65(2)	60 <b>Nd</b> neodymium 144.24(3)	61 <b>Pm</b> promethium [144.9127]	62 <b>Sm</b> samarium 150.36(3)	63 <b>Eu</b> europium 151.964(1)	64 <b>Gd</b> gadolinium 157.25(3)	65 <b>Tb</b> terbium 158.925 34(2)	66 <b>Dy</b> dysprosium 162.500(1)	67 <b>Ho</b> holmium 164.930 32(2)	68 <b>Er</b> erbium 167.259(3)	69 <b>Tm</b> thulium 168.934 21(2)	70 <b>Yb</b> ytterbium 173.04(3)	71 <b>Lu</b> lutetium 174.967(1)
			89 <b>Ac</b> actinium [227.0277]	90 <b>Th</b> thorium 232.0381(1)	91 <b>Pa</b> protactinium 231.036 88(2)	92 <b>U</b> uranium 238.028 91(3)	93 <b>Np</b> neptunium [237.0482]	94 <b>Pu</b> plutonium [244.0642]	95 <b>Am</b> americium [243.0614]	96 <b>Cm</b> curium [247.0704]	97 <b>Bk</b> berkelium [247.0703]	98 <b>Cf</b> californium [251.0796]	99 <b>Es</b> einsteinium [252.0830]	100 <b>Fm</b> fermium [257.0951]	101 <b>Md</b> mendelevium [258.0964]	102 <b>No</b> nobelium [259.1010]	103 <b>Lr</b> lawrencium [262.1097]

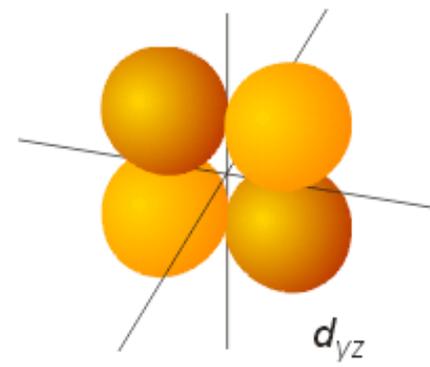
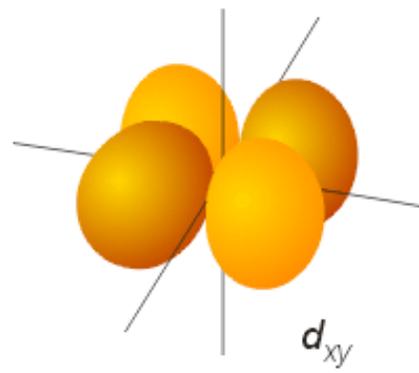
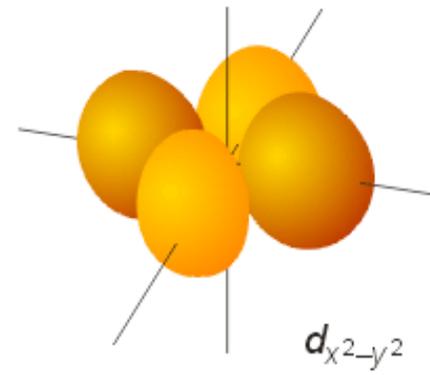
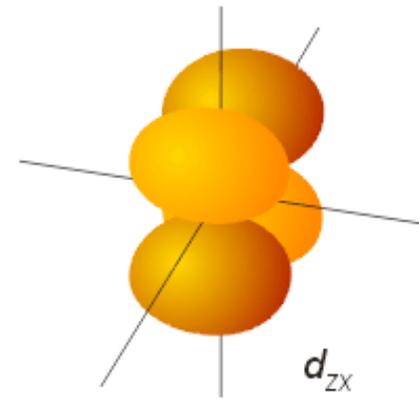
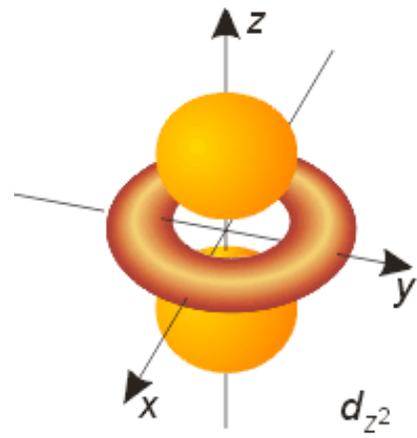
## Notes

- IUPAC alternative names or spelling exist for the elements aluminium (aluminum) and caesium (cesium) and, in special circumstances, sodium (natrium), potassium (kalium), iron (ferrum), copper (cuprum), silver (argentum), tin (stannum), antimony (stibium), tungsten (wolfram), gold (aurum), mercury (hydrargyrum), and lead (plumbum).
- Relative atomic masses ('atomic weights') of elements with no IUPAC assigned standard values are listed between square brackets. IUPAC 2001 standard values are given for other elements, with uncertainties in the last figure in parentheses [R. Loss, Pure Appl. Chem. 75, 1107-1122 (2003)].
- Element with atomic number 111 has not yet been named. The IUPAC provisional name is shown.
- Claims for the existence of elements with atomic numbers 112, 114, and 116 have not been recognized by IUPAC as of August 2003.

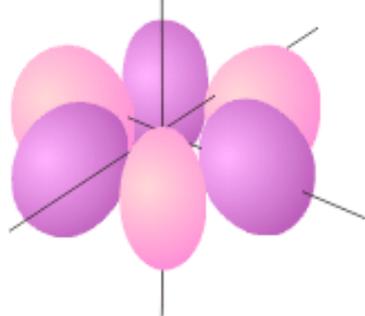




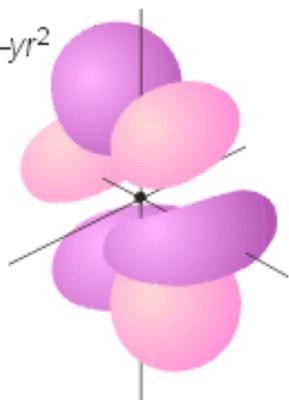




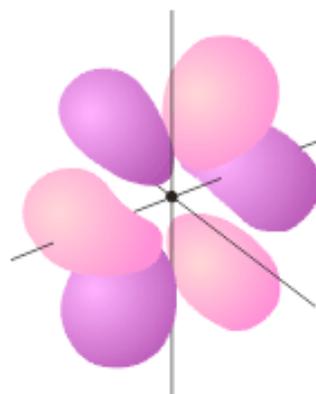
$$4f_{y^3-3yx^2}$$



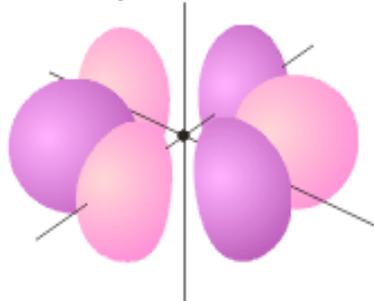
$$4f_{5yz^2-yr^2}$$



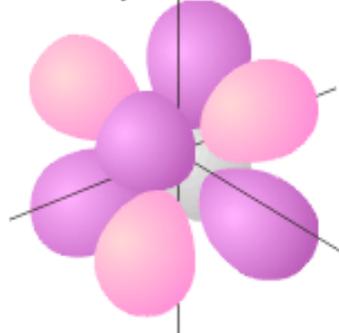
$$4f_{5xz^2-3xr^2}$$



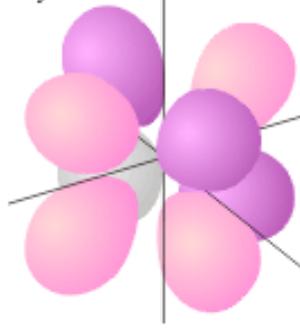
$$4f_{x^3-3xy^2}$$



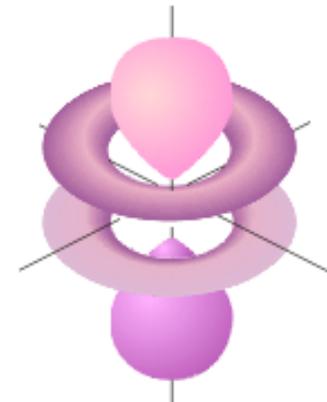
$$4f_{zx^2-zy^2}$$

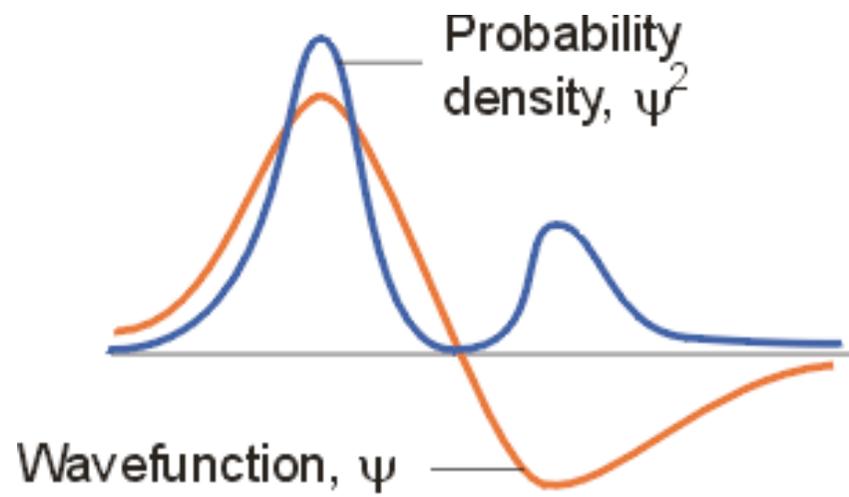


$$4f_{xyz}$$



$$4f_{5z^3-3zr^2}$$





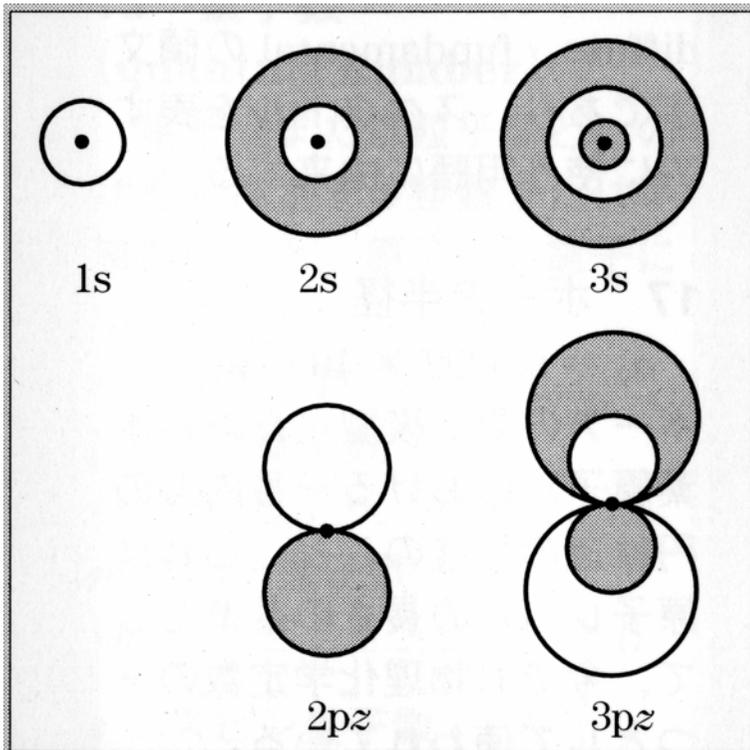
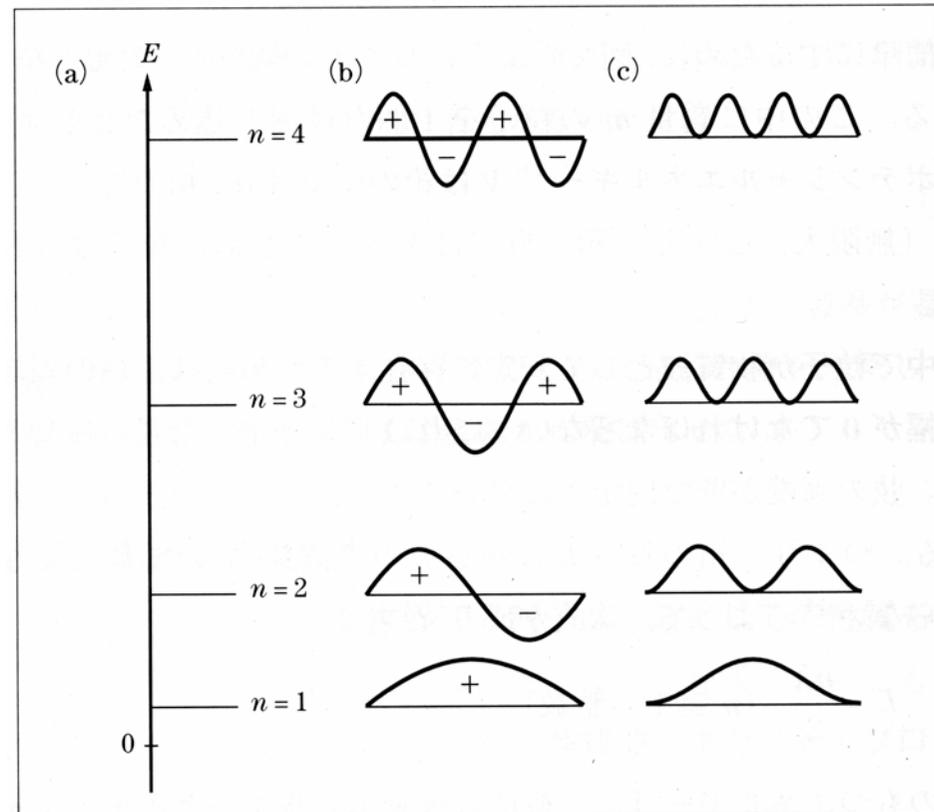


図6 軌道の空間分布の模式図  
 (白は正, 黒は負, 中央の黒丸は原子核)



一次元の箱の中の粒子

(a) エネルギー準位, (b) 波動関数  $\Psi$ , (c) 存在密度  $|\Psi|^2$

$$c = v \times \lambda$$

$$E = h \times v = h \times \frac{c}{\lambda}$$

$c$   
 $\lambda$

$c$ : 光速、 $h$ : プランク定数  
 $v$ : 振動数、 $\lambda$ : 波長

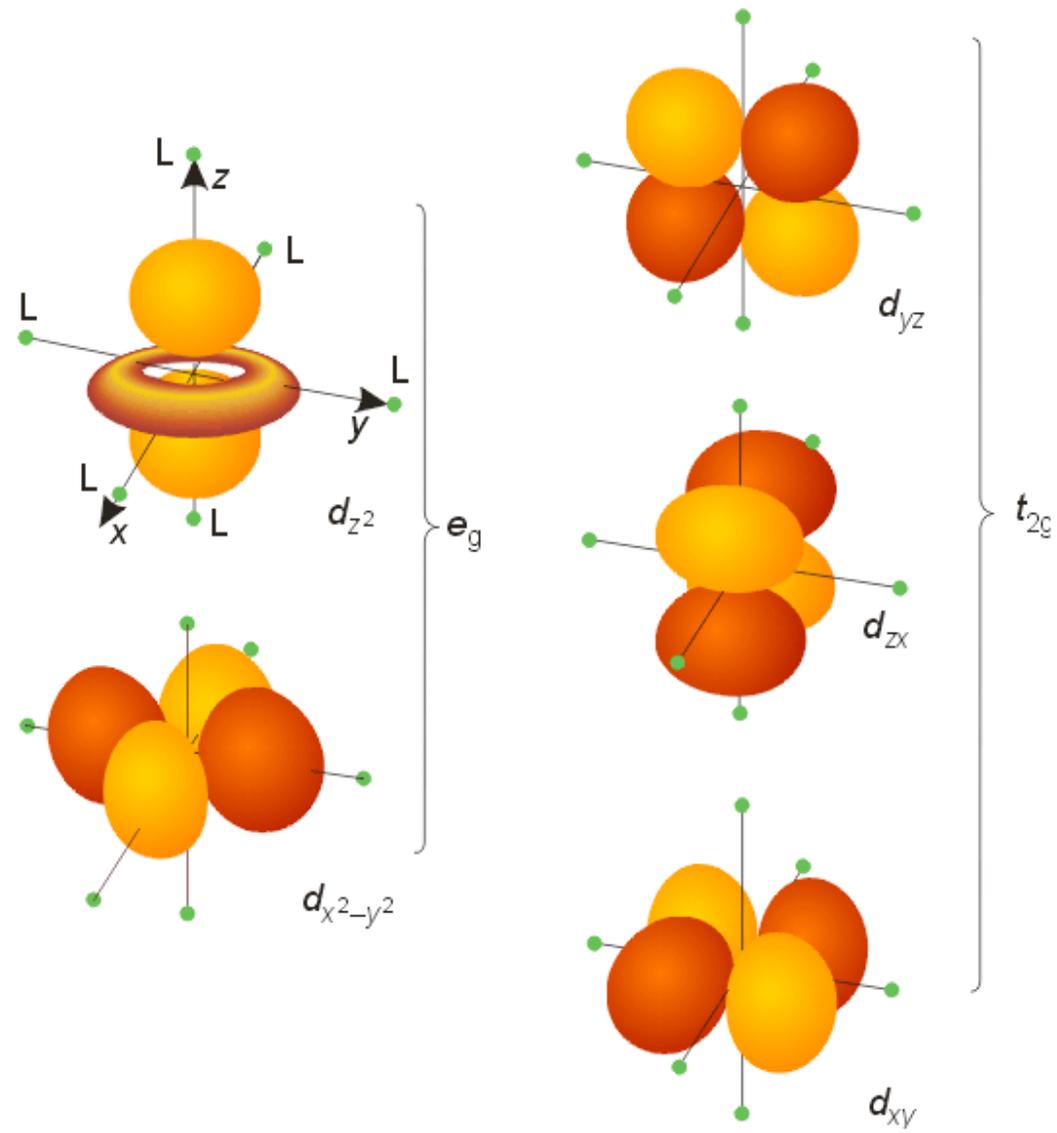
## 炭素(C)とケイ素(Si)の違い

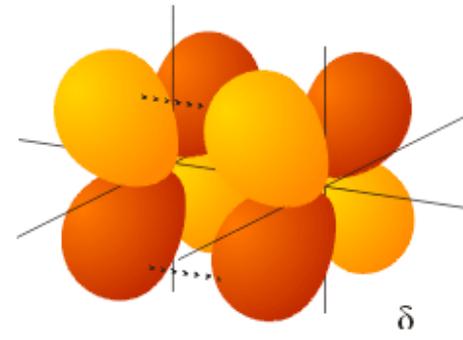
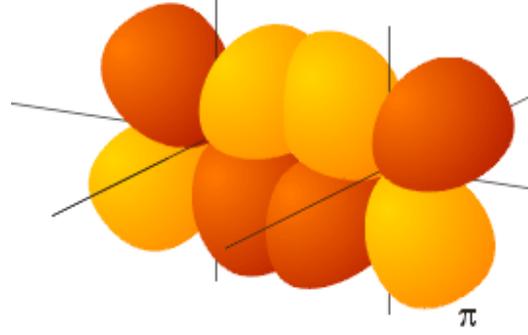
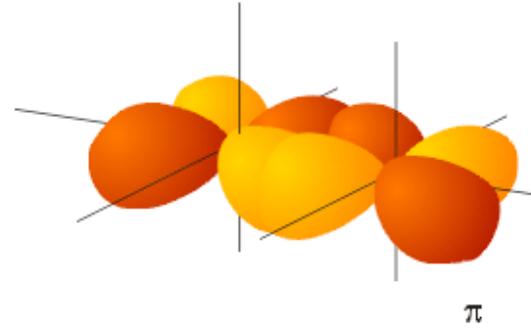
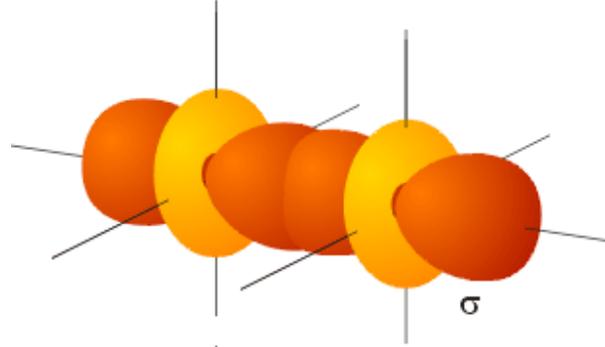
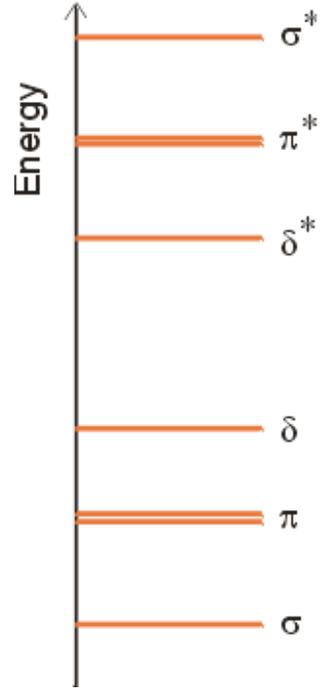
C: 多重結合性(二重、三重結合)

Si: 単結合(多重結合は希)

C:  $(1s)^2(2s)^2(2p)^2$

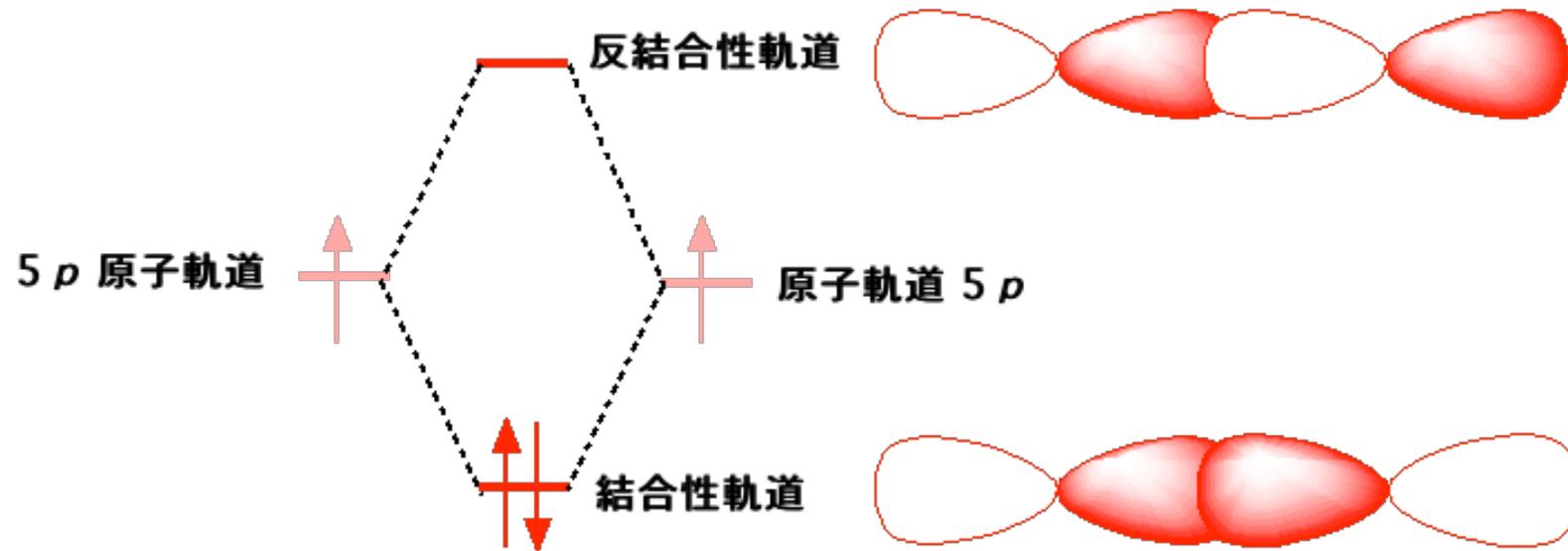
Si:  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$





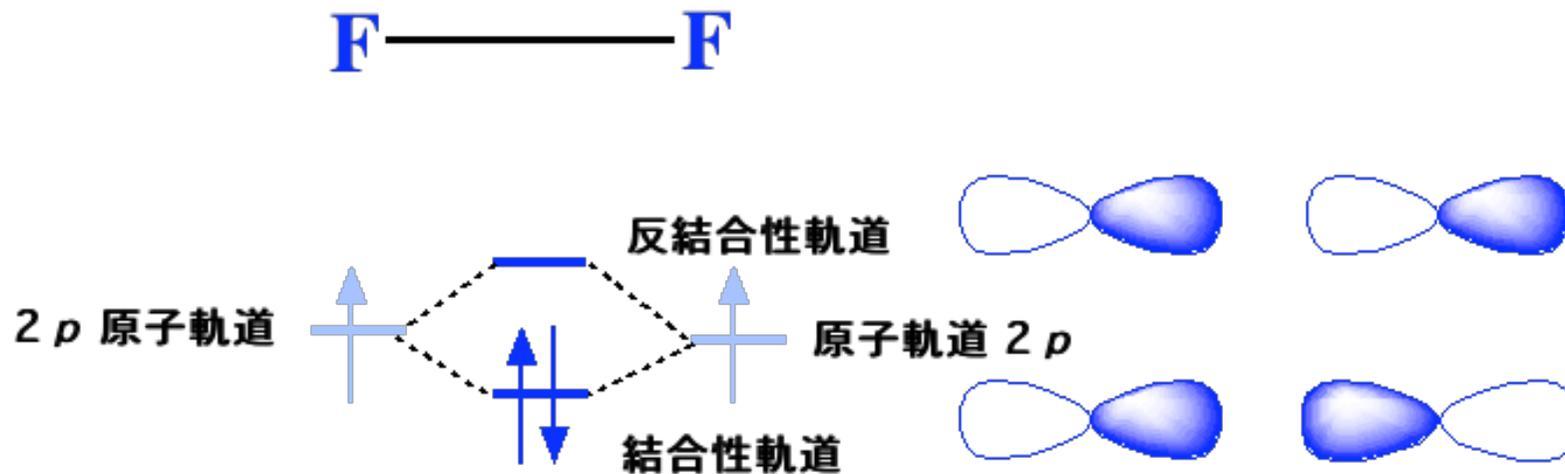
# 軌道（波動関数）の広がり

共有結合性：大 ( $I_2$ )



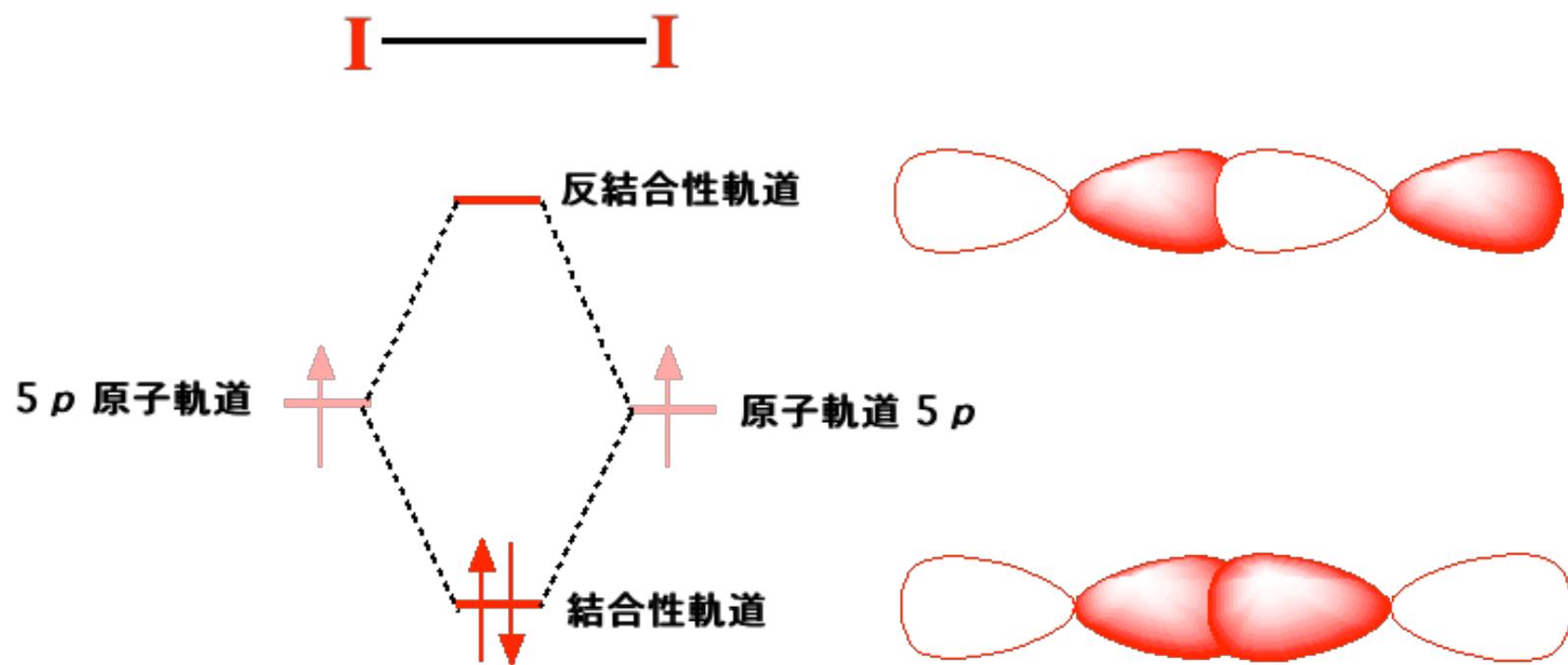
# 軌道（波動関数）の広がり

共有結合性：小 ( $F_2$ )



# 軌道（波動関数）のエネルギー差

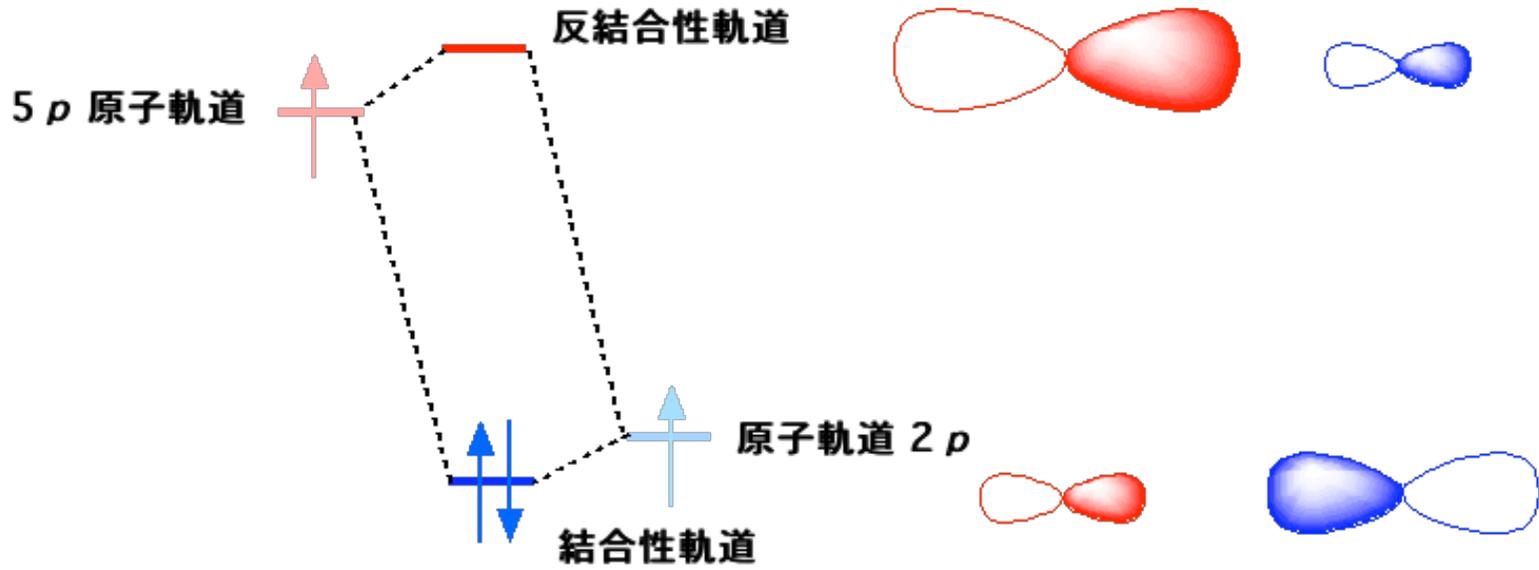
共有結合性：大 ( $I_2$ )



# 軌道（波動関数）のエネルギー差

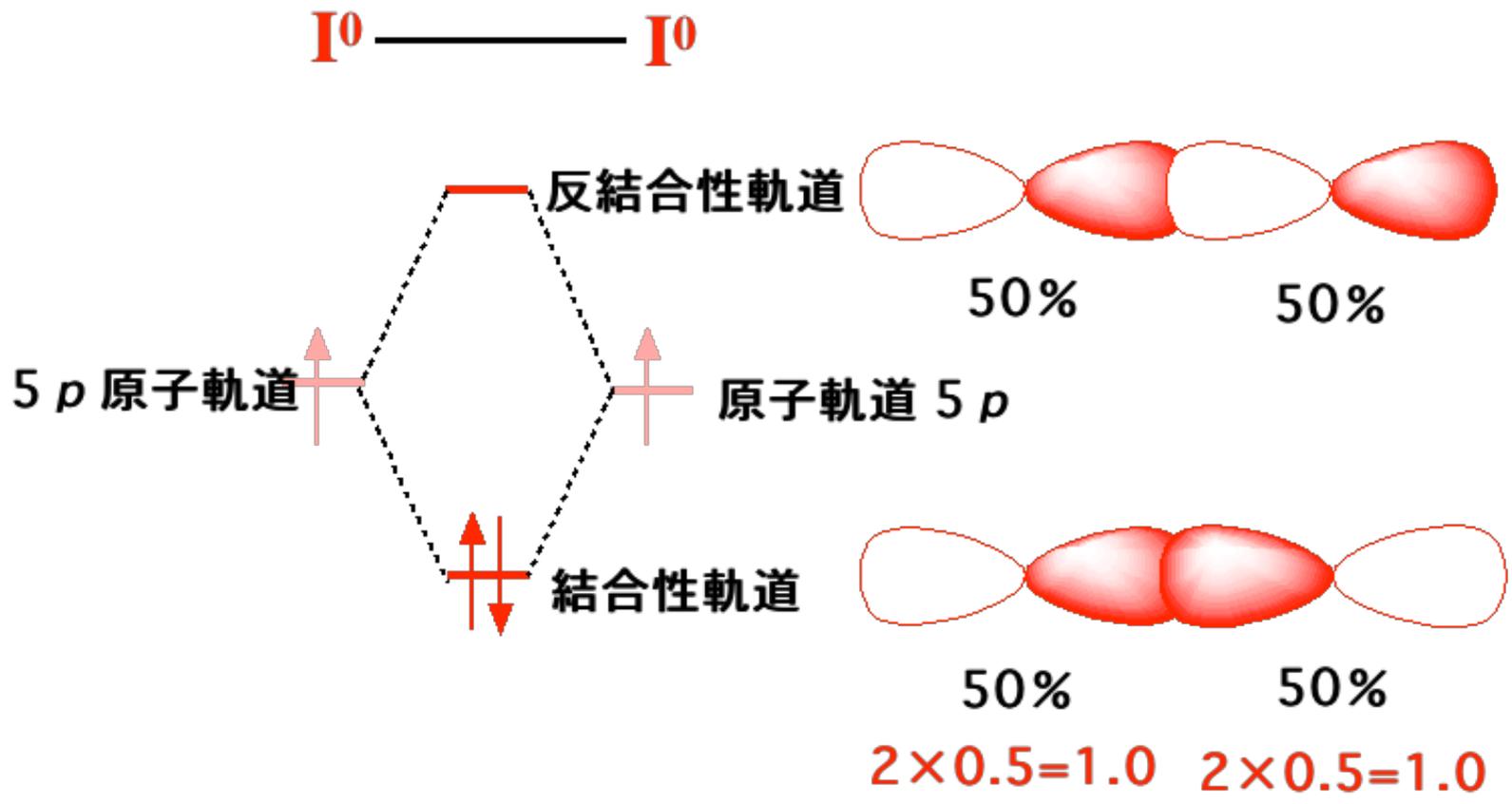
共有結合性：小 (I-F)

I ————— F



# 無極性と極性

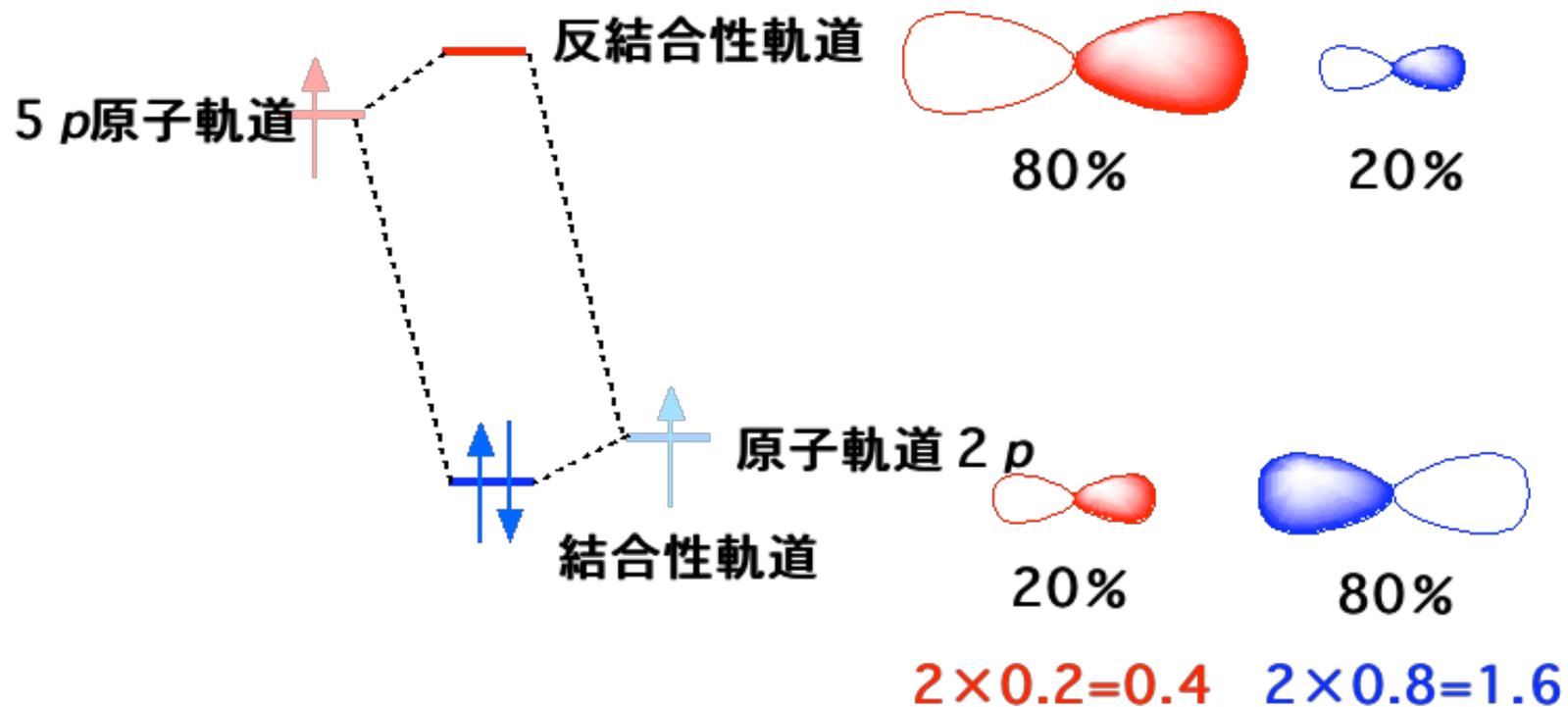
極性：無 ( $I_2$ )



# 無極性と極性

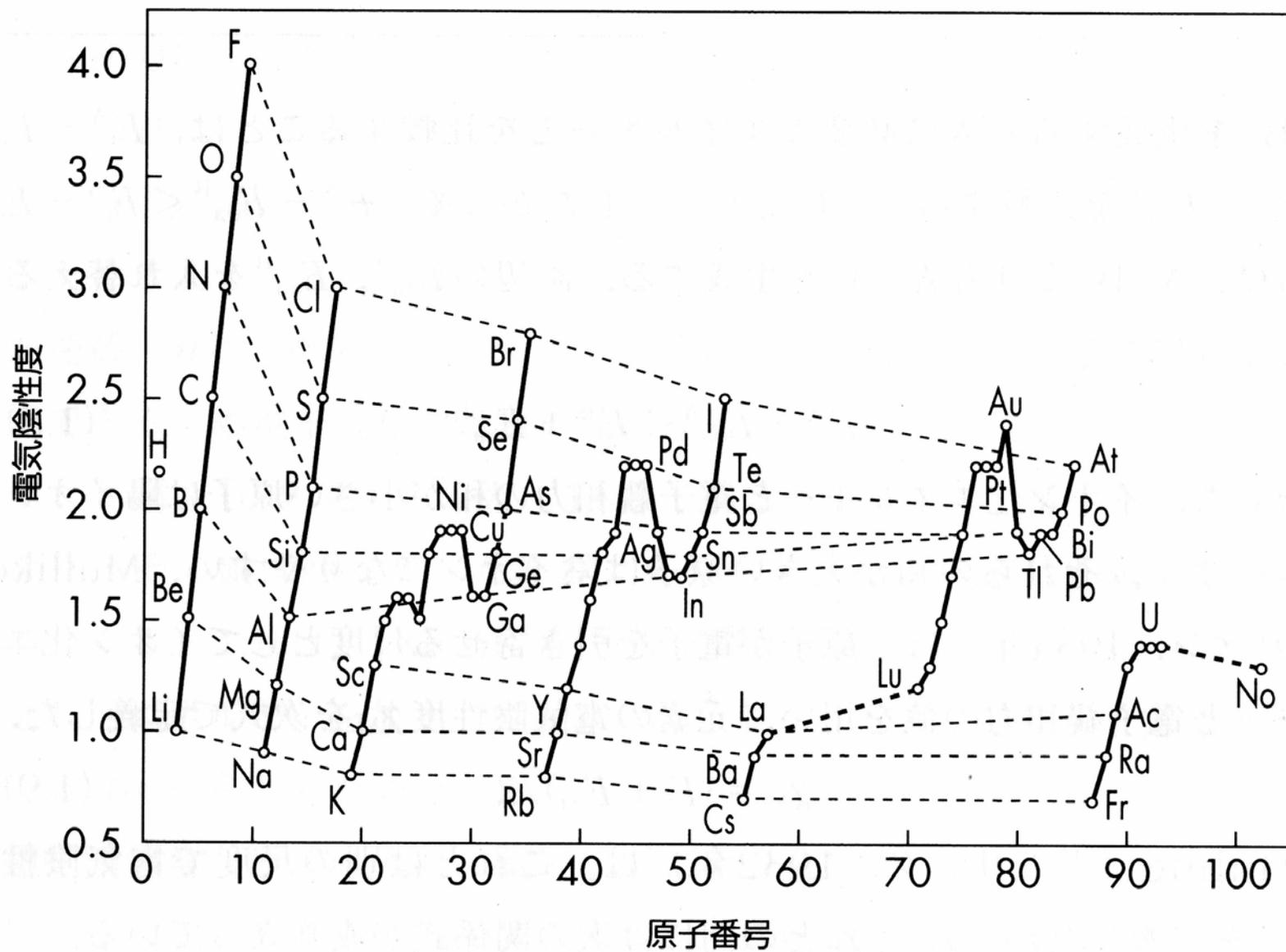
極性：有 (I-F)

I<sup>0.6+</sup> ————— F<sup>0.6-</sup>

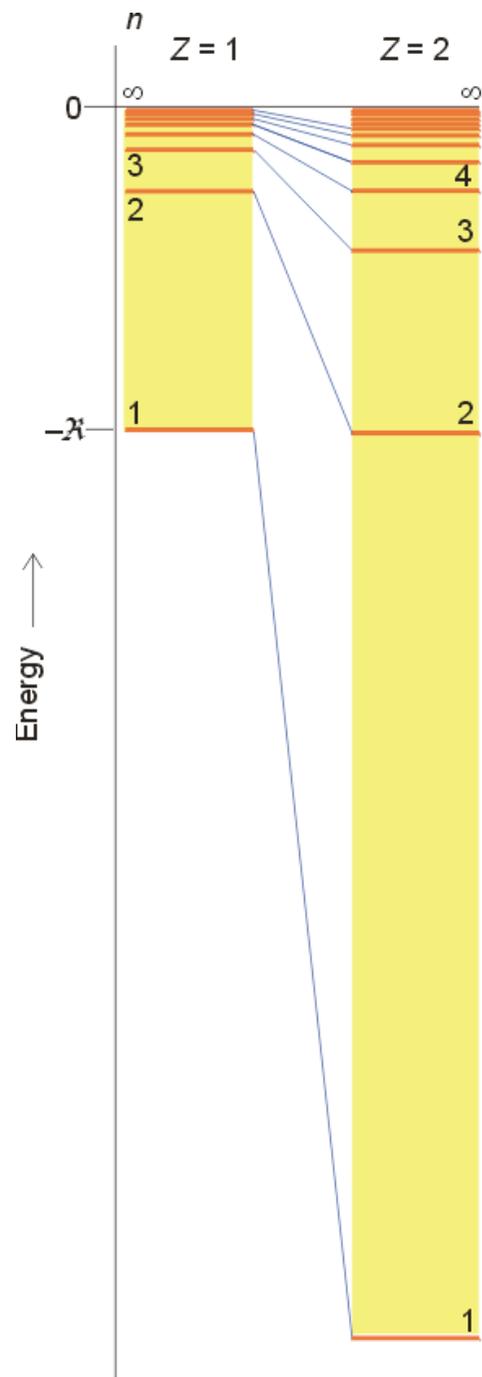


原子軌道間のエネルギー差があれば、

結合には必ず極性が生じる



電気陰性度の周期性.



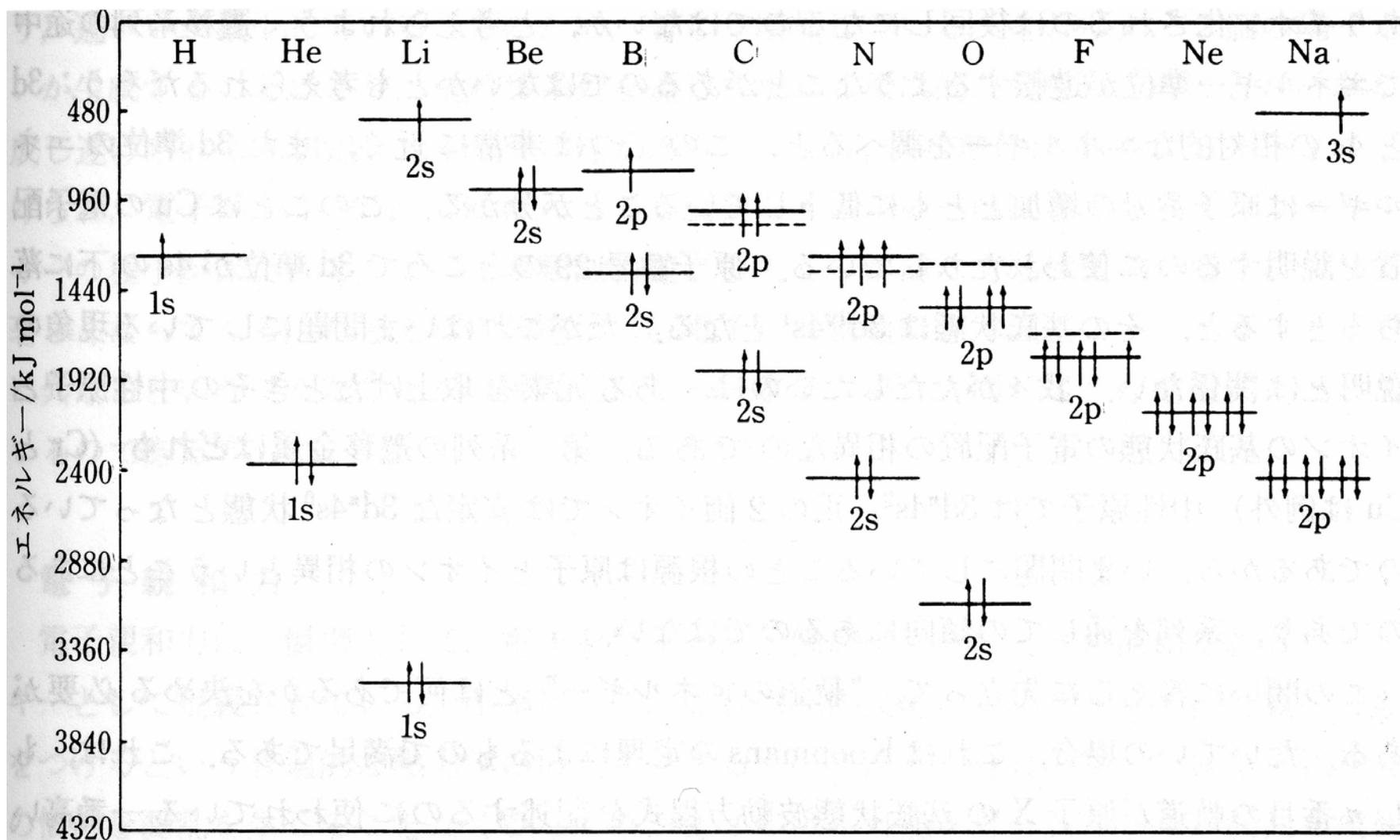
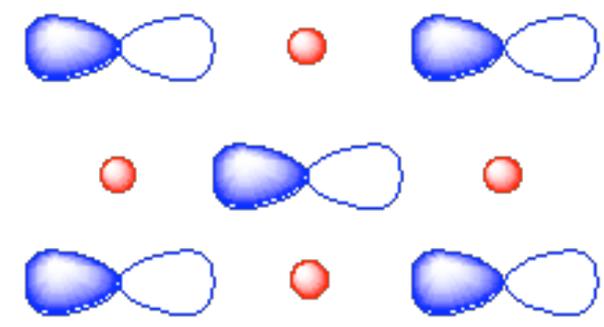
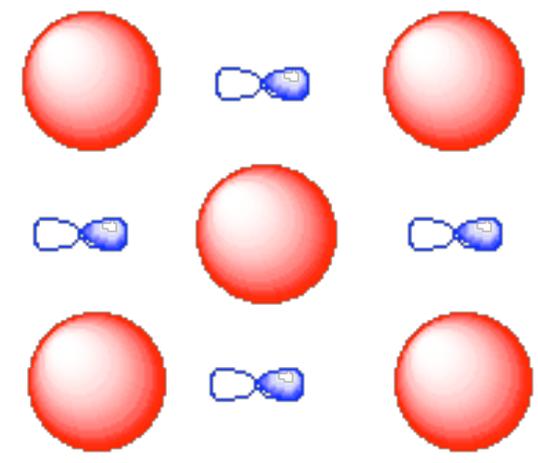
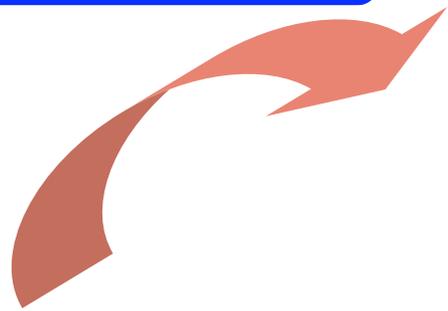
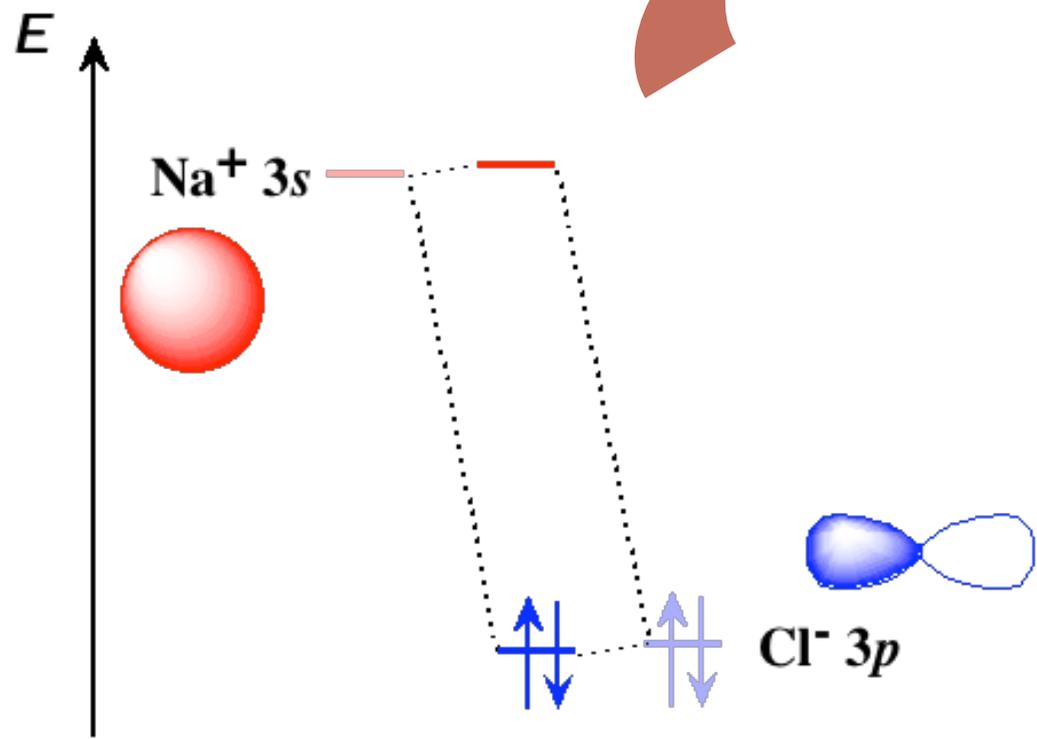
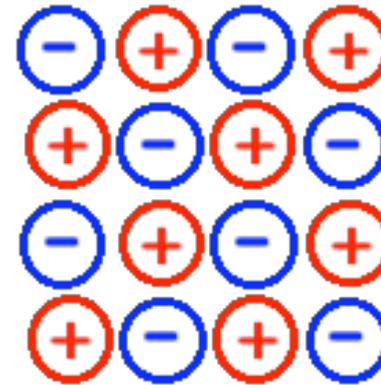
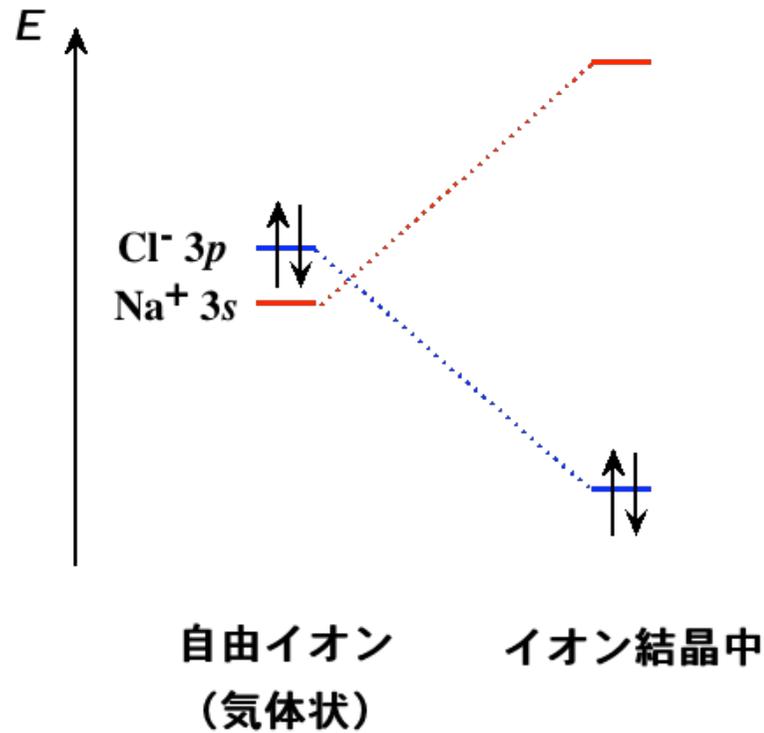


図 2・14 水素からナトリウムまでの軌道エネルギーの相対値. 実線は一電子軌道エネルギーを示す. 点線は実測されたイオン化エネルギーを示す. 後者は電子-電子の相互作用のため実線で示されたものと異なっている

イオン結合：  
静電相互作用（クーロン相互作用）



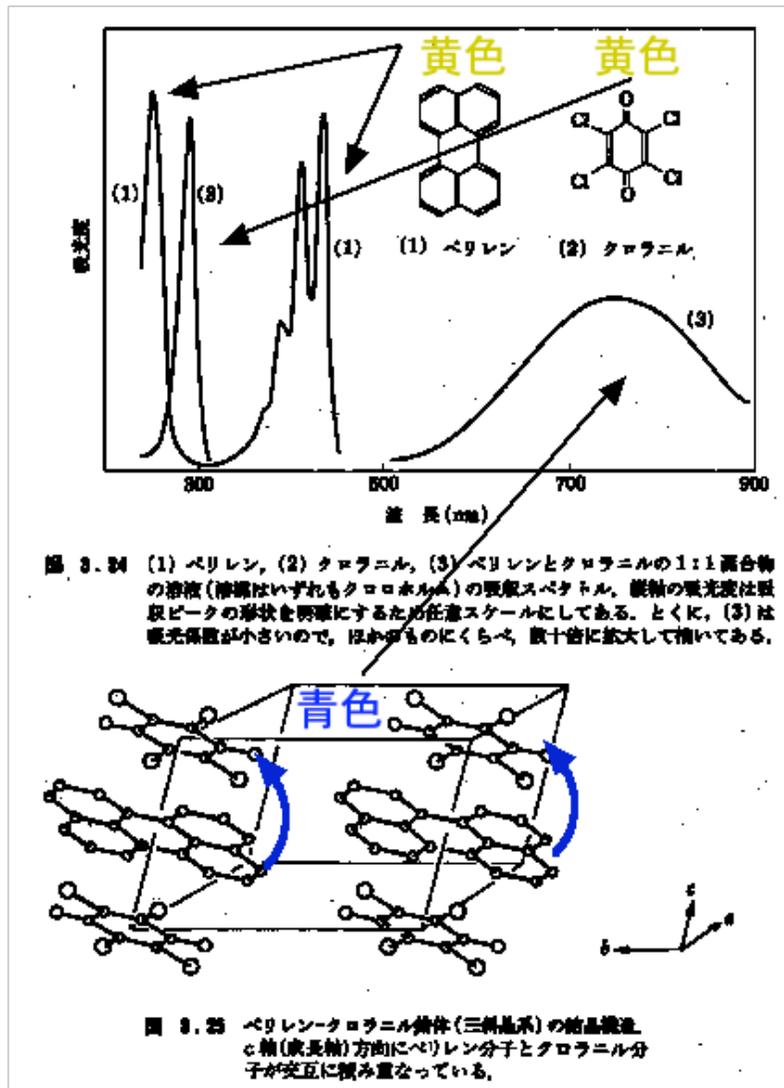
イオン結合：  
静電相互作用（クーロン相互作用）



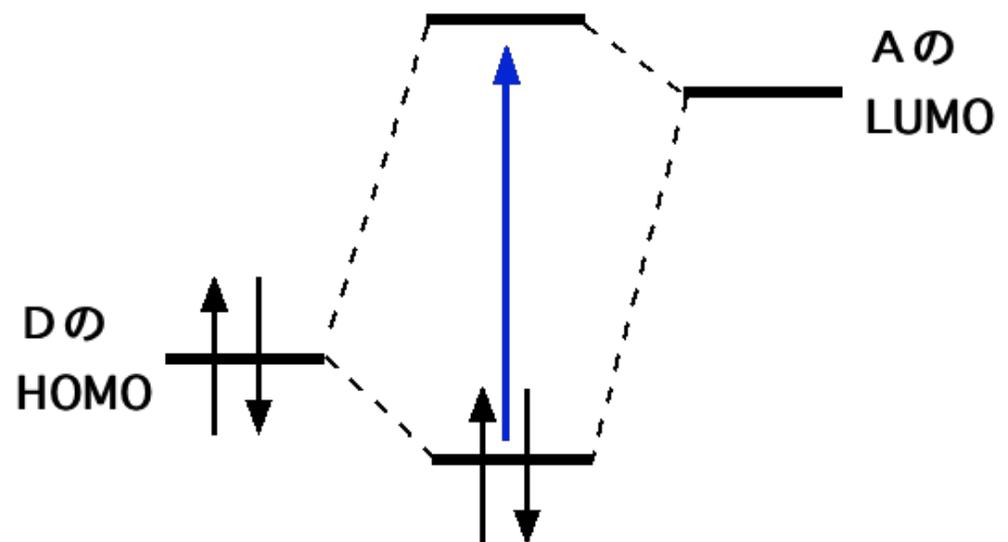
マードルングポテンシャル

# 電荷移動相互作用(charge-transfer interaction)とは？

電荷移動錯体(charge-transfer complex; CT complex)



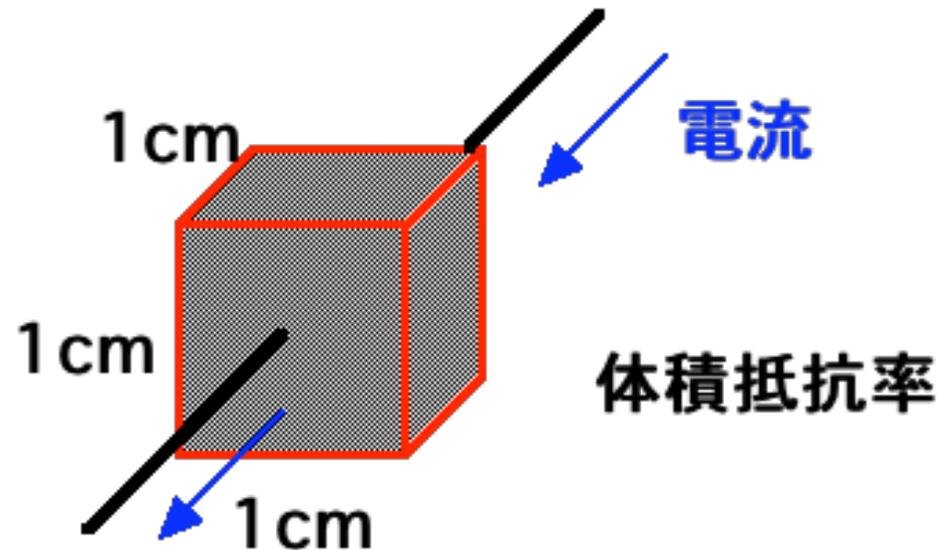
ドナー (D) : 電子供与体 --- ペリレン  
 アクセプター (A) : 電子受容体 --- クロラニル

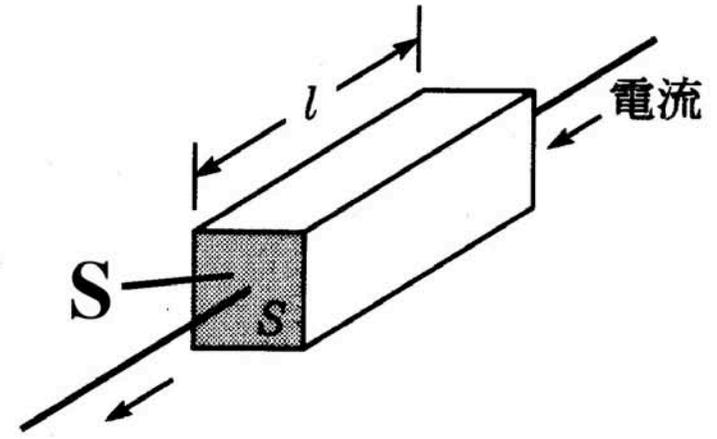
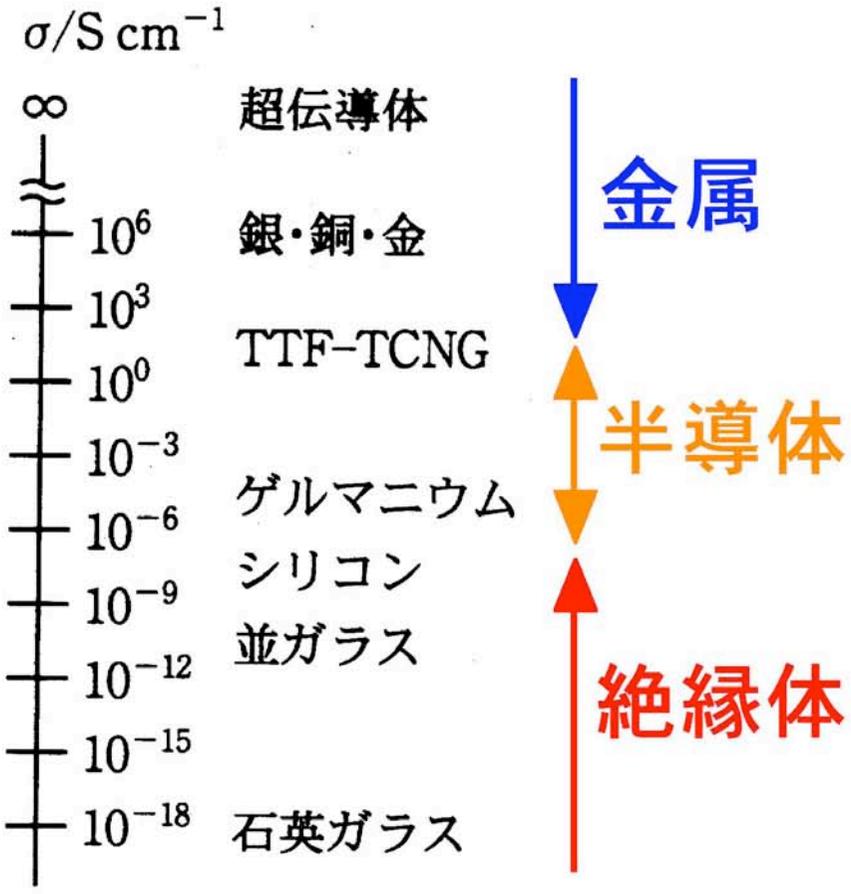


金属(metal)、半導体(semiconductor)、  
絶縁体(insulator)とは？

電気抵抗率： $\rho$  ( $\Omega\text{cm}$ )

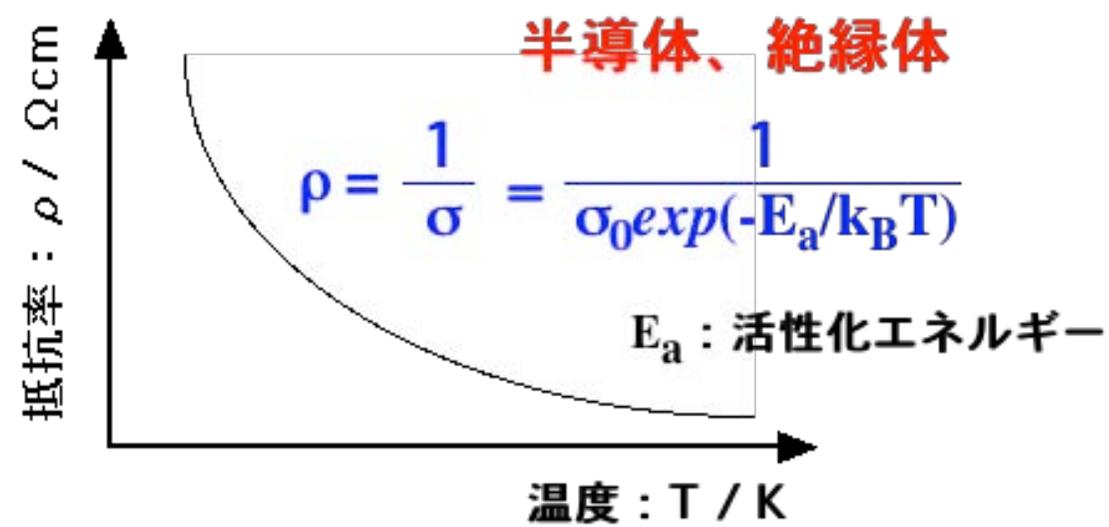
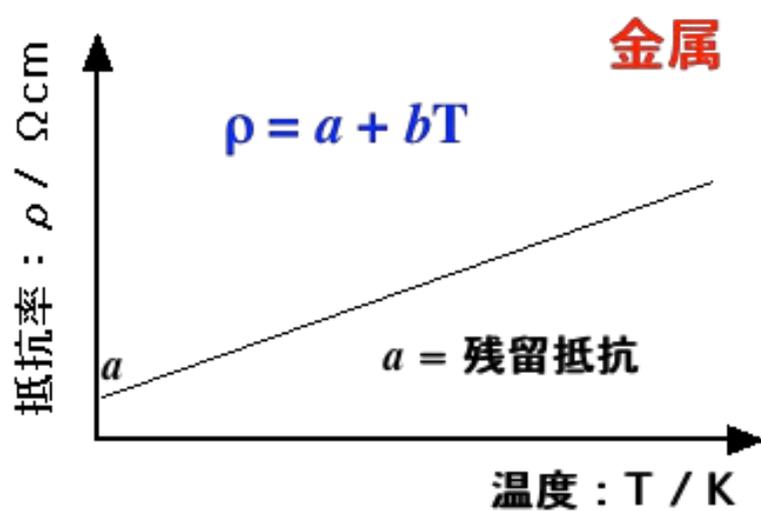
電気伝導度： $\sigma$  ( $\Omega^{-1}\text{cm}^{-1} = \text{S cm}^{-1}$ ) =  $\rho^{-1}$

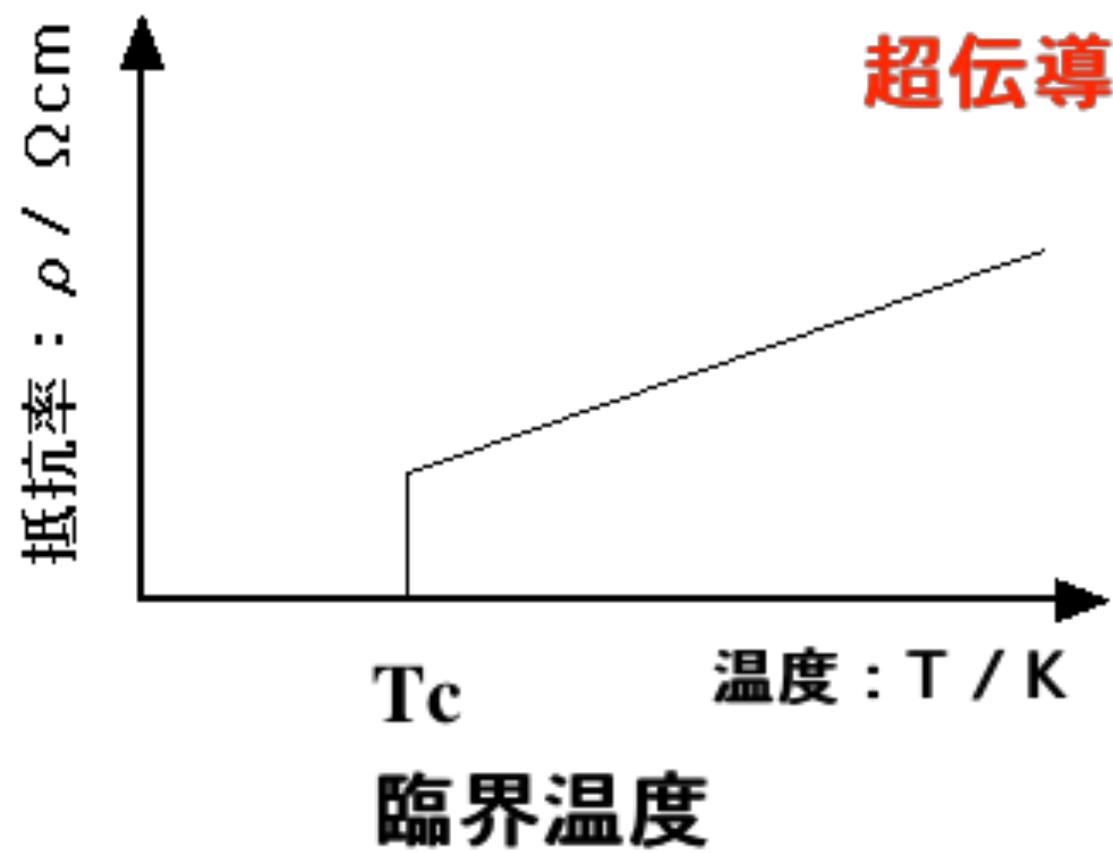


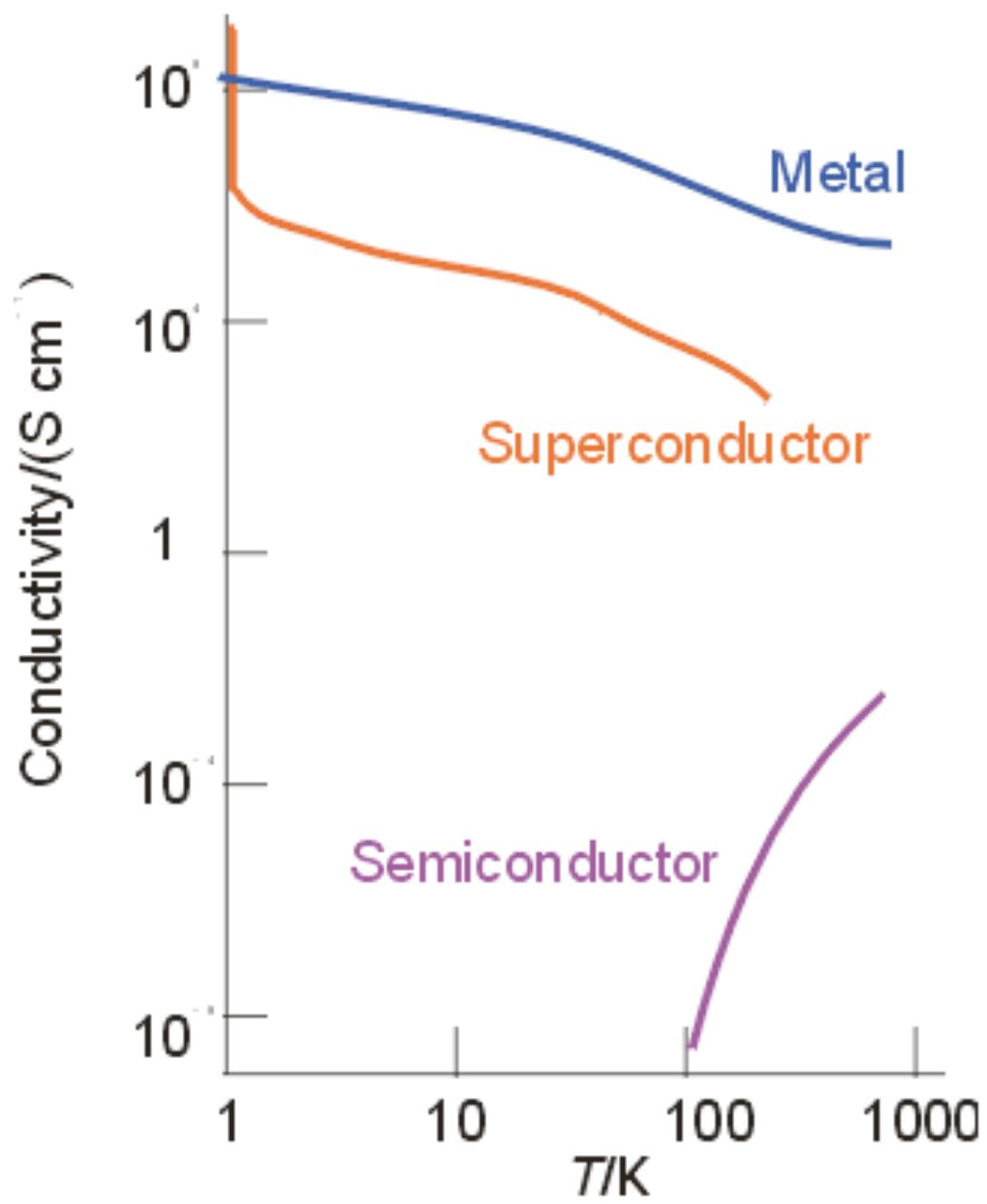


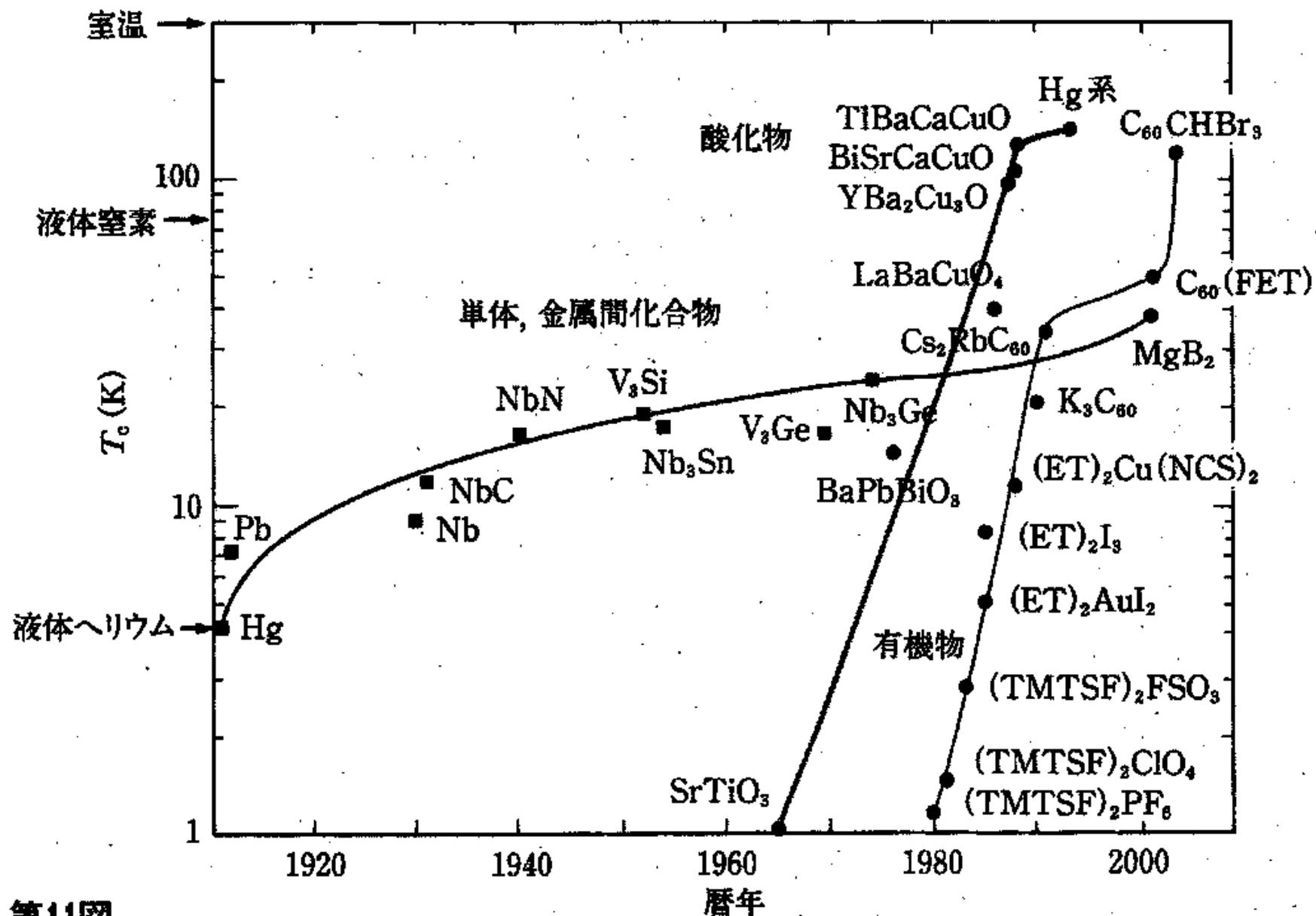
$$\rho = R \times \frac{S}{l}$$

$$= \frac{V}{I} \times \frac{S}{l}$$





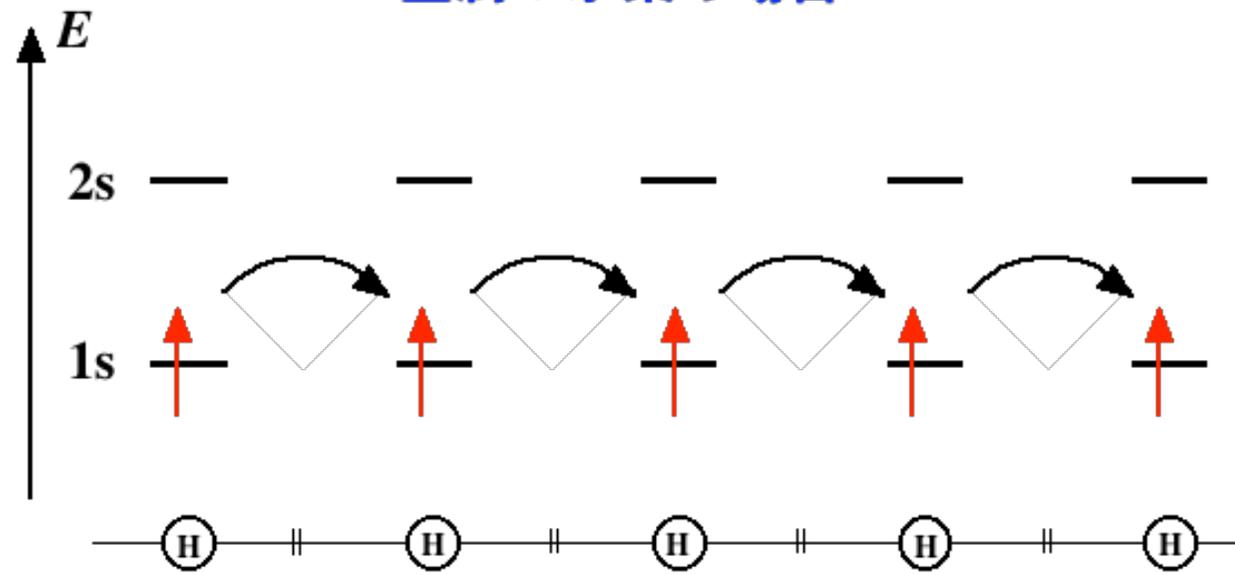




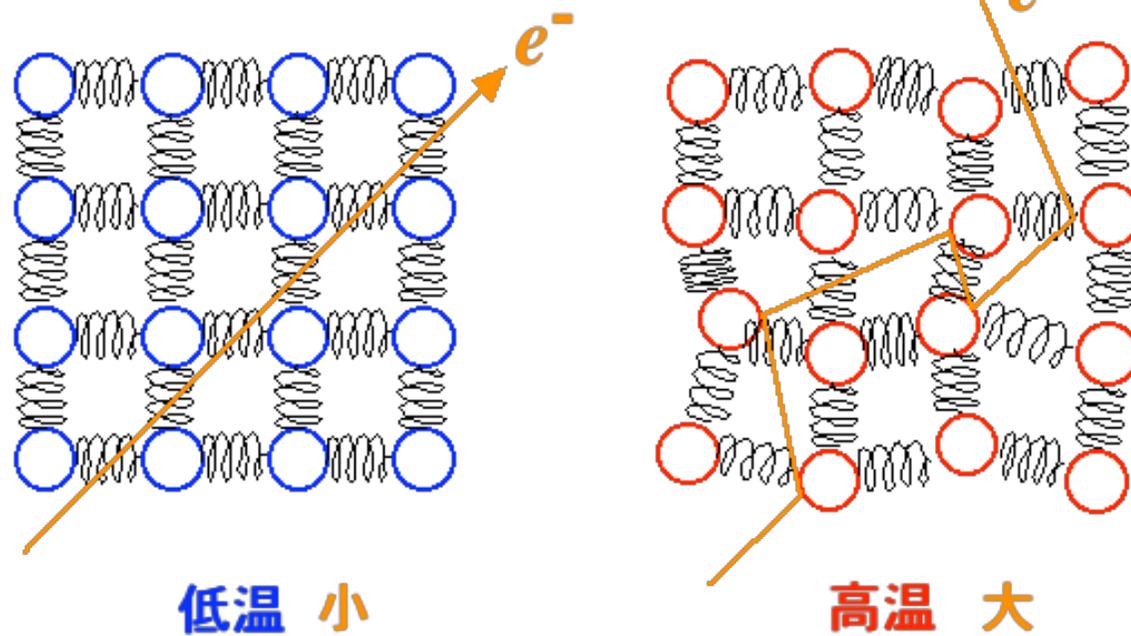
第11図

様々なカテゴリーの物質の超伝導転移温度が年(横軸)とともに上昇する様子。

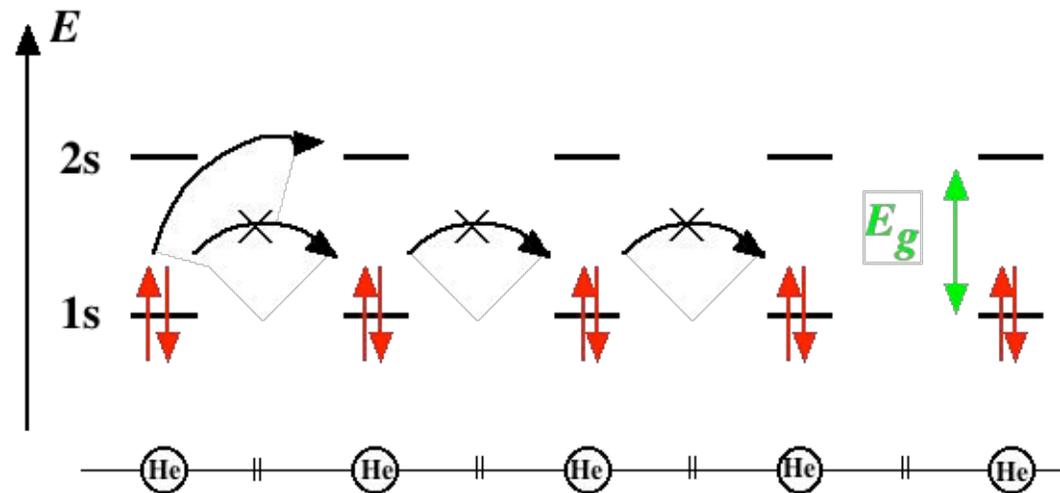
# 金属：水素の場合



## 格子振動による散乱



## 半導体：ヘリウムの場合



伝導度： $\sigma = n e \mu$

$n$ ：キャリアー数

$e$ ：電気素量

$\mu$ ：移動度

$E_g$ の存在：熱活性型

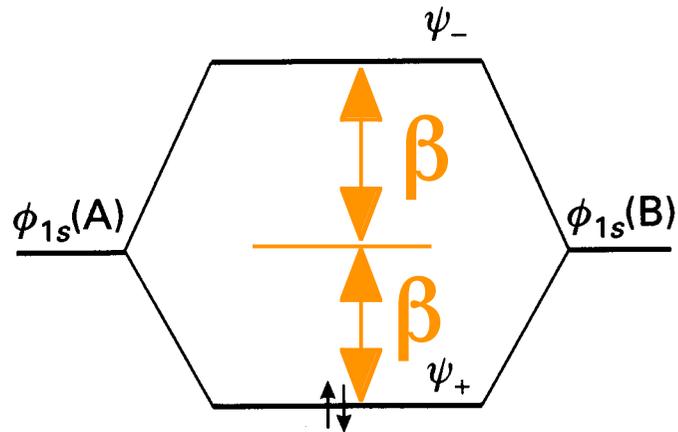
キャリアー数

低温：少

高温：多

# バンドとは

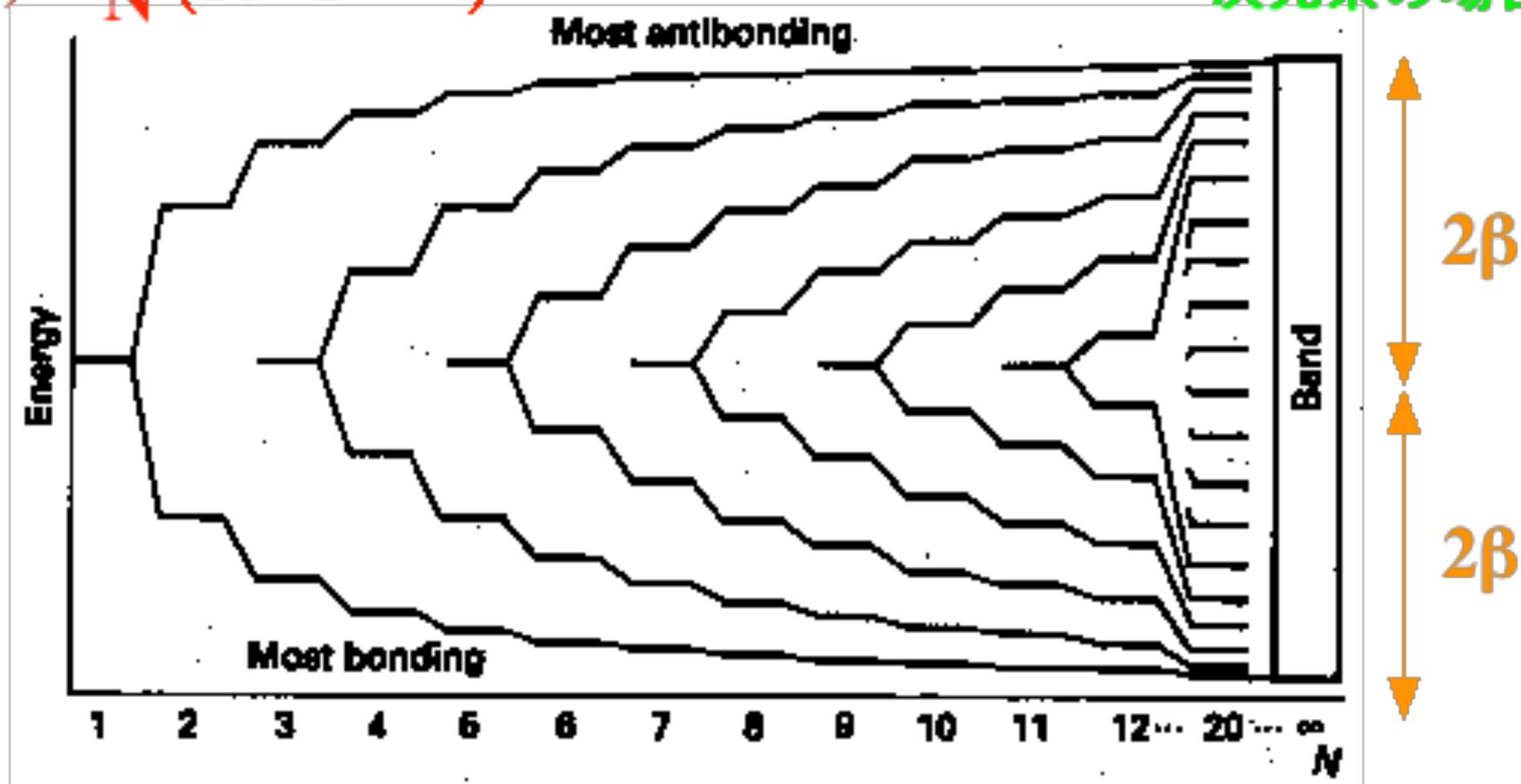
## (1) $H_2$

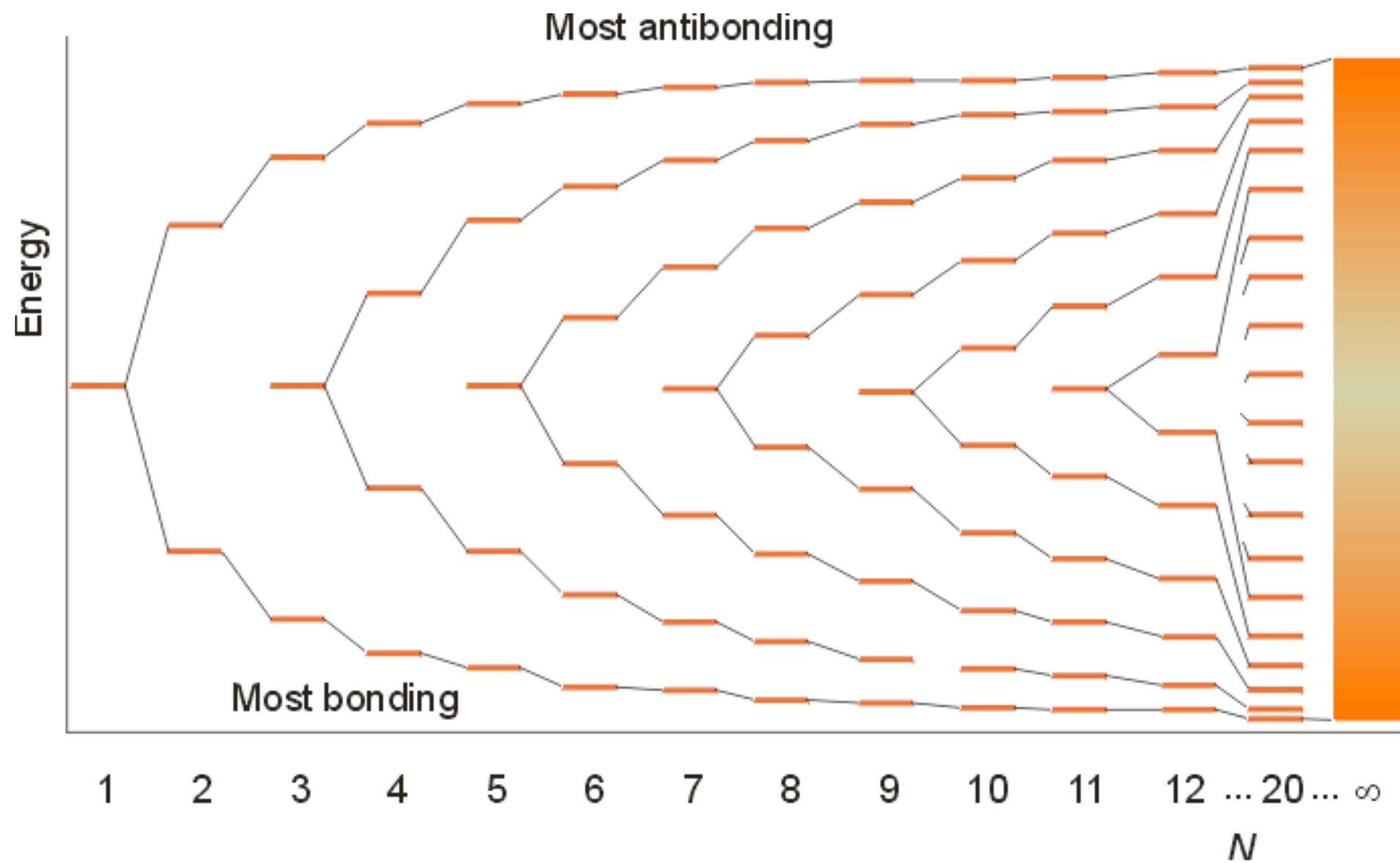


$\beta$  : 相互作用(共鳴)積分

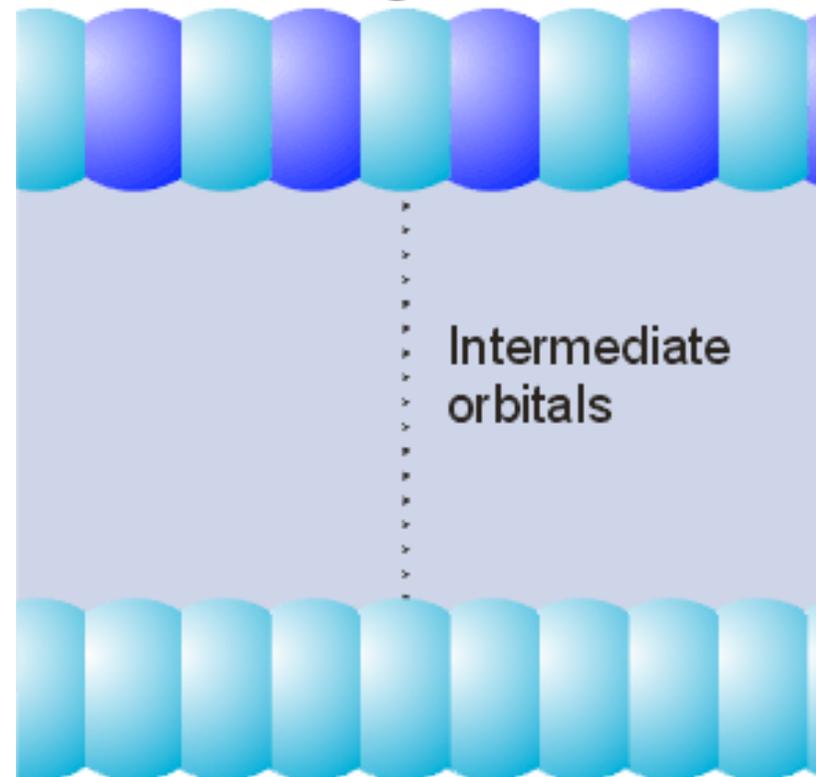
(2)  $H_N$  ( $N=1 \sim \infty$ )

一次元系の場合

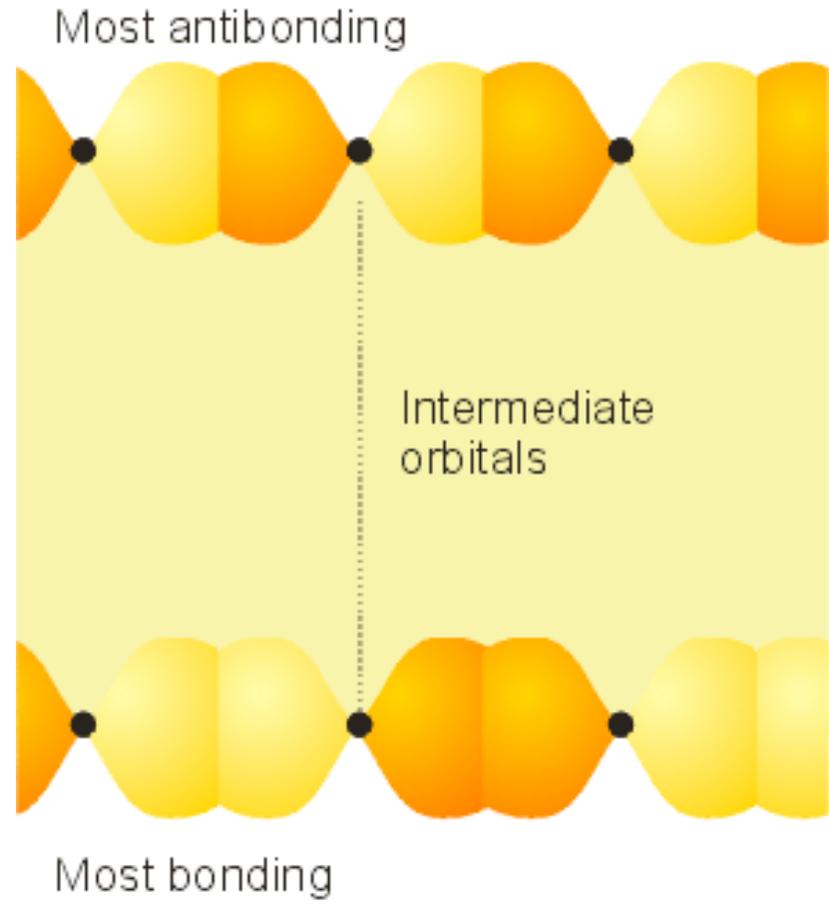


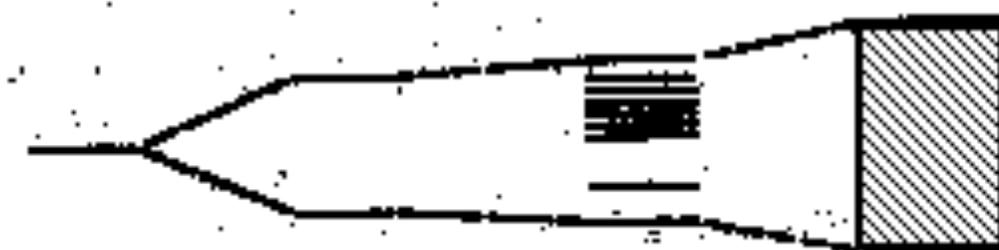
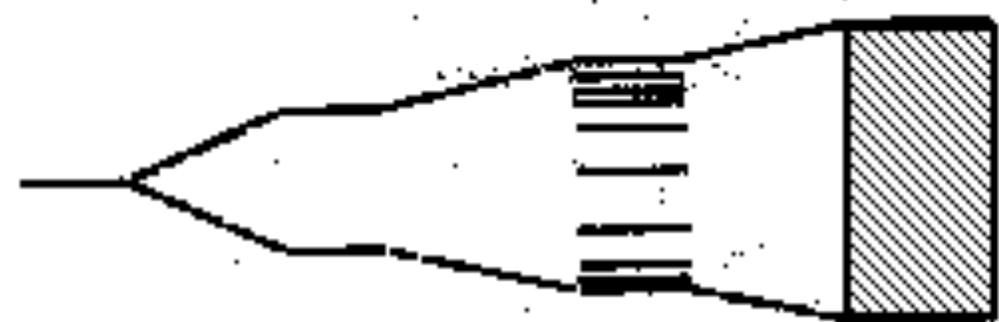


Most antibonding



Most bonding

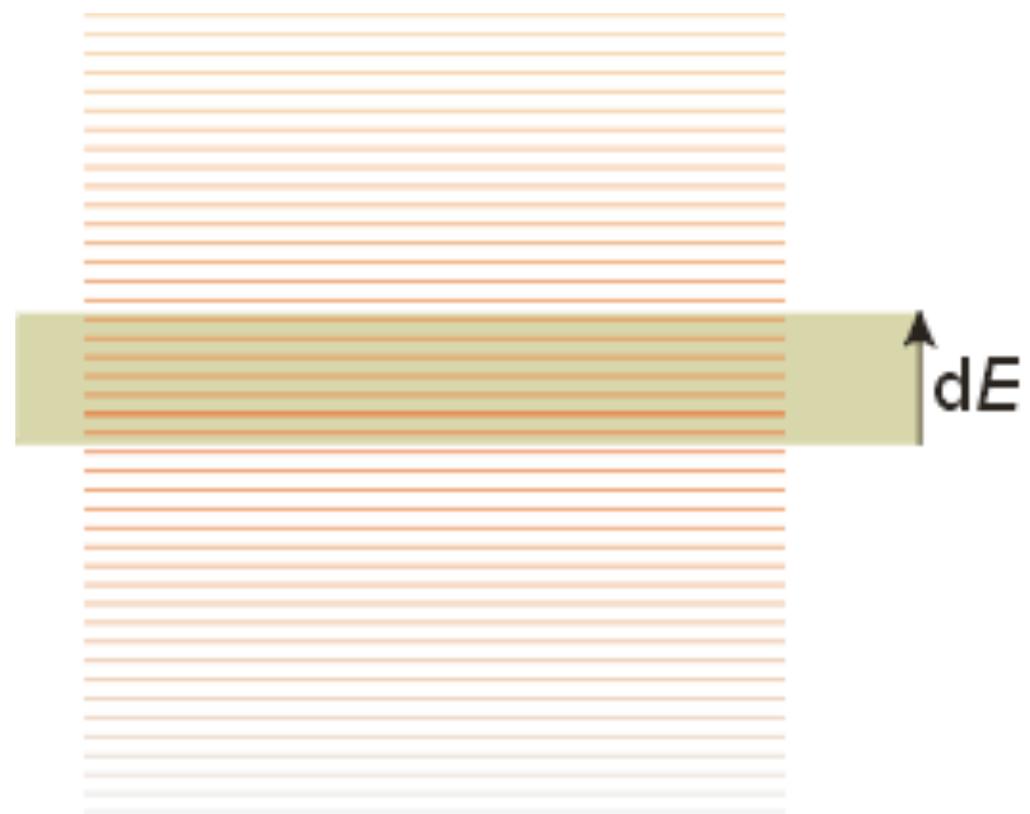


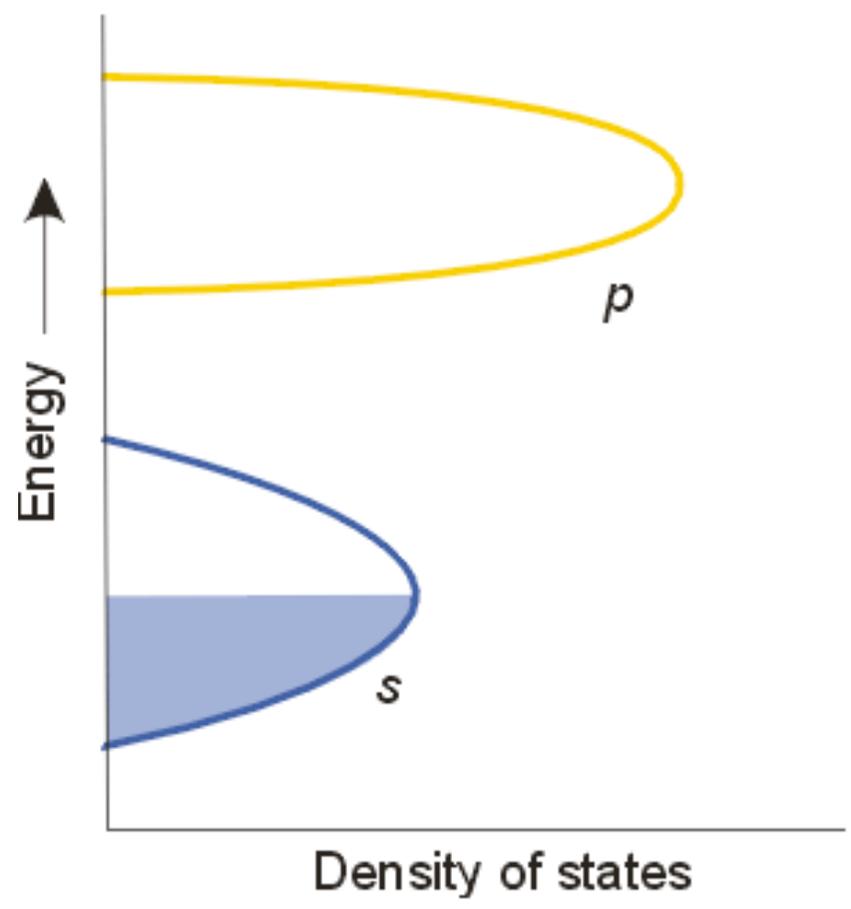


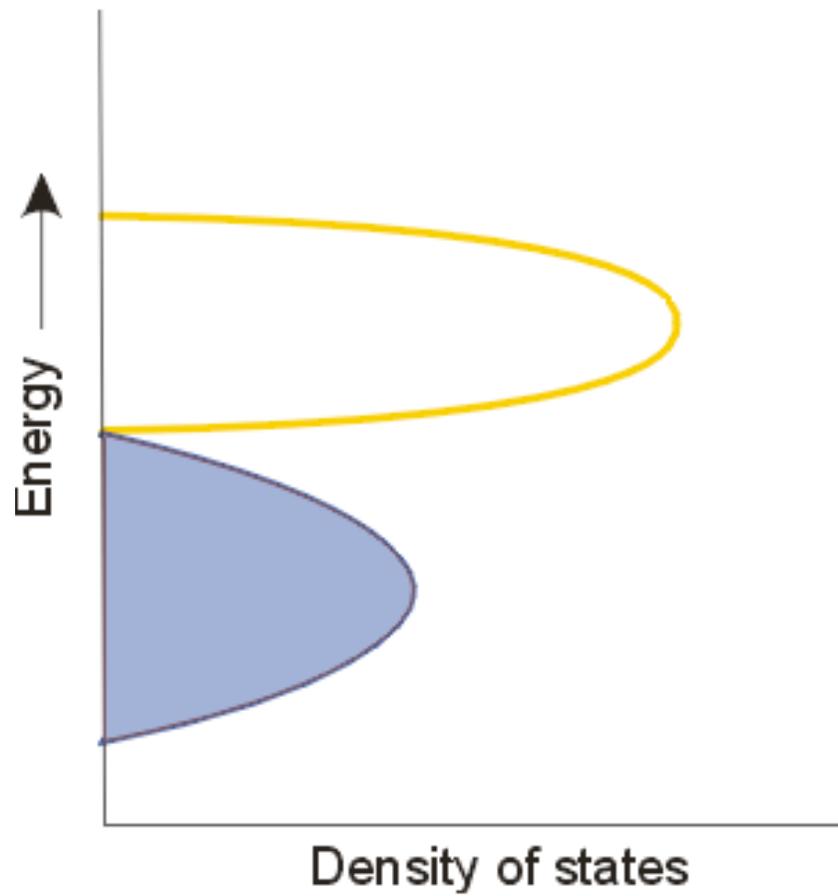
状态密度

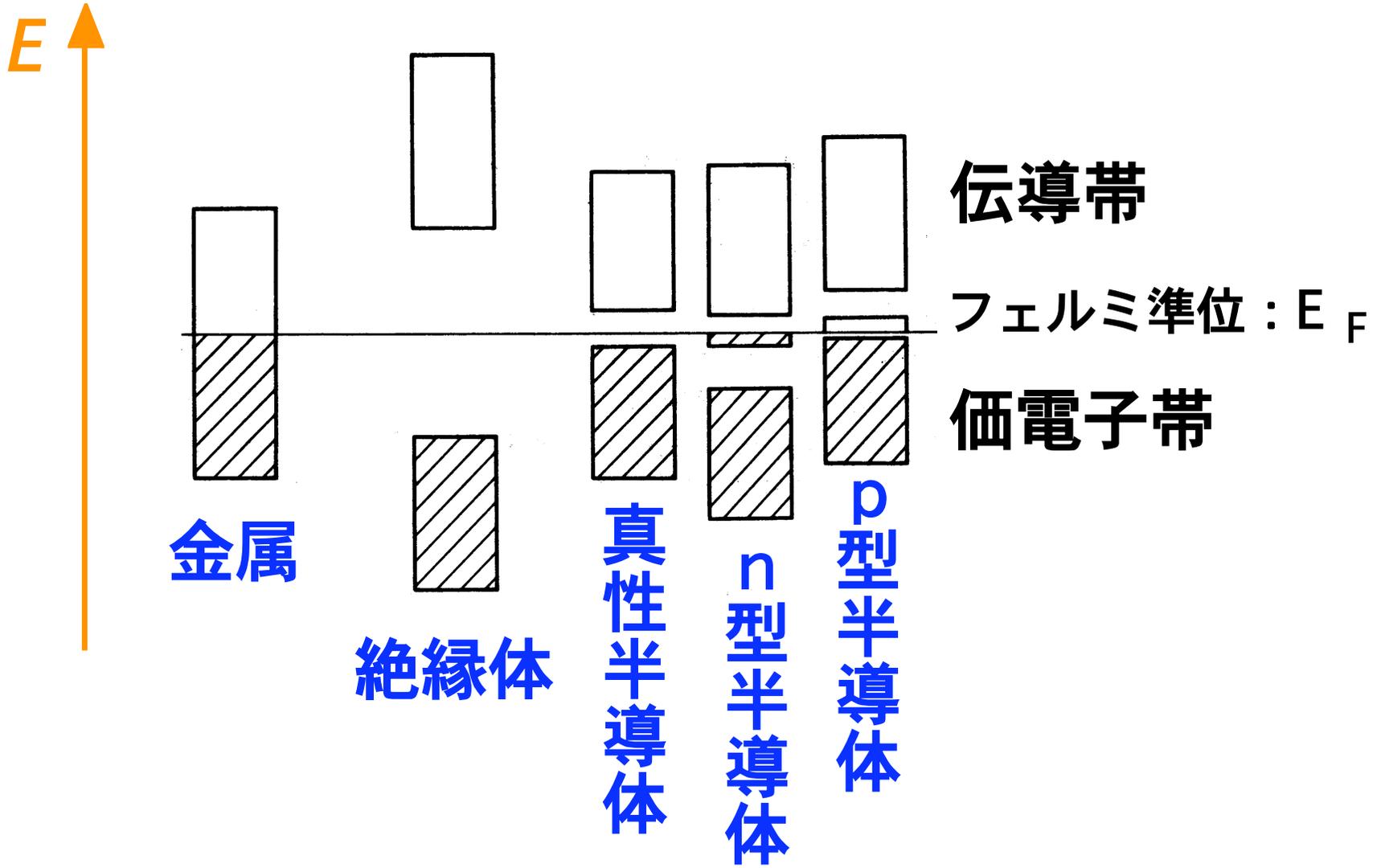
$\rho(E)$

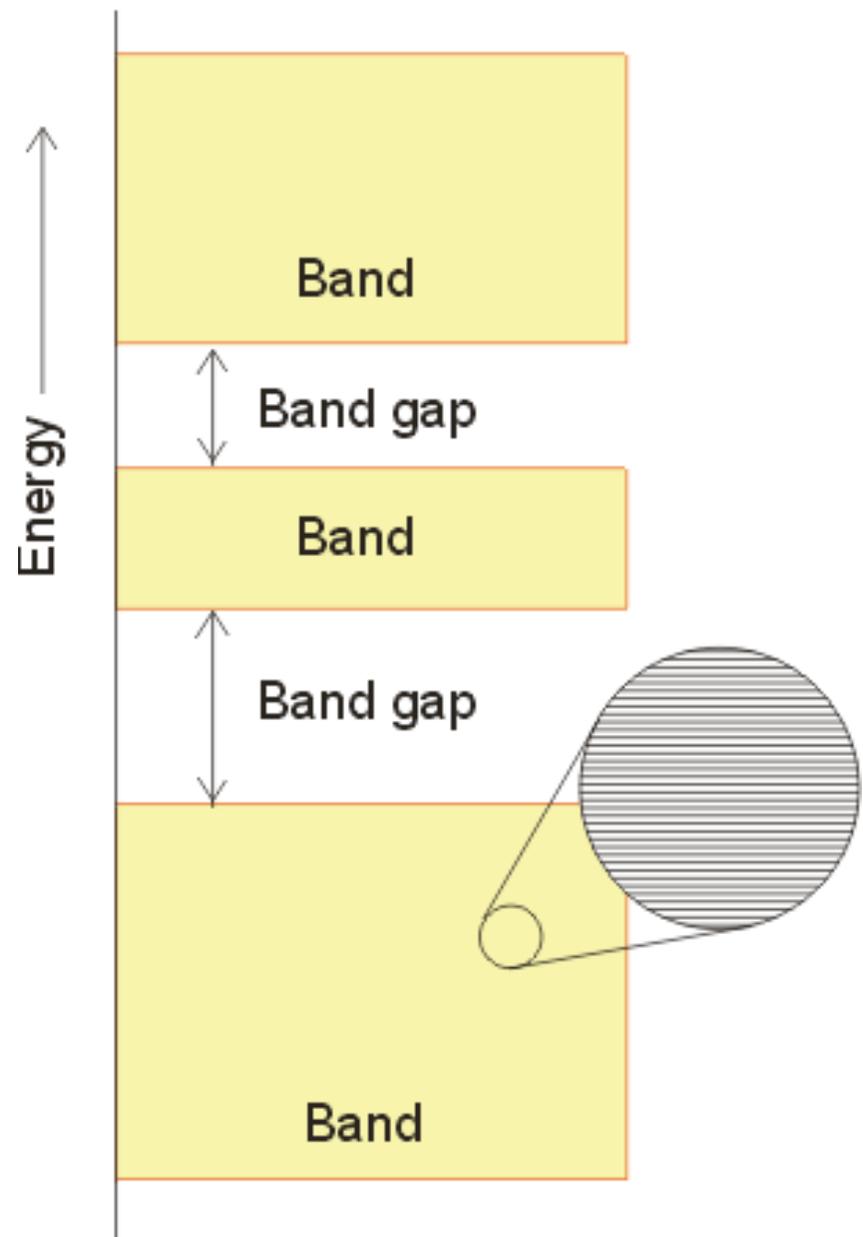
原子    分子    大分子    固体



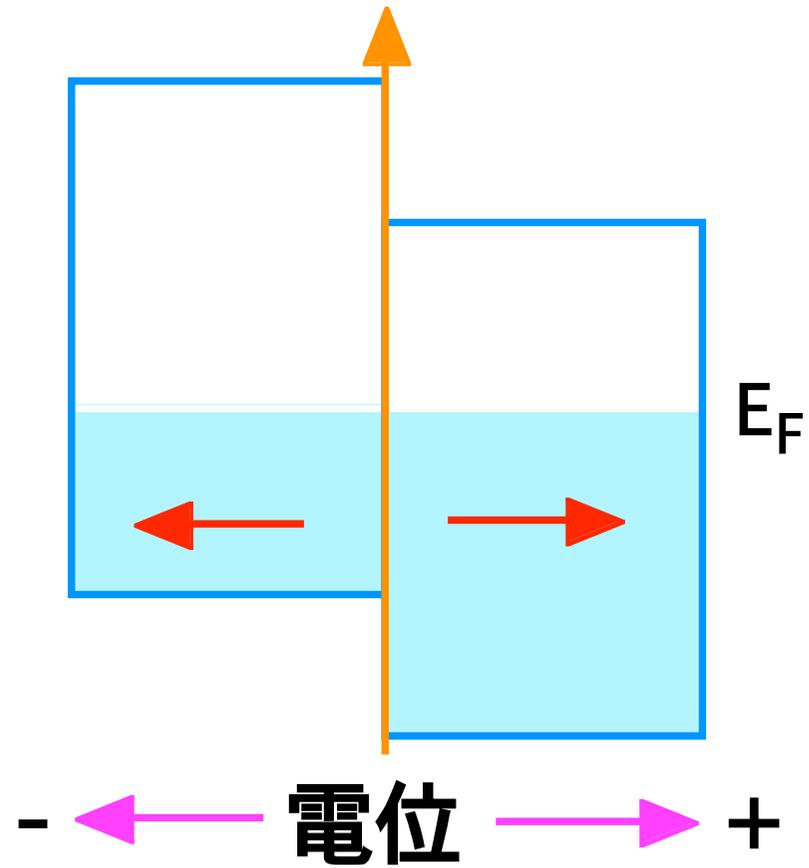
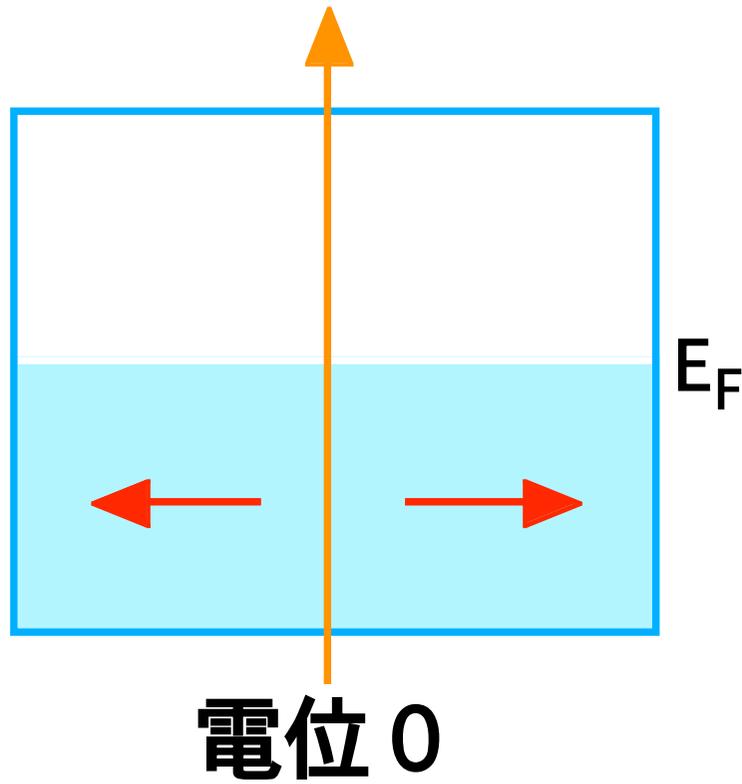


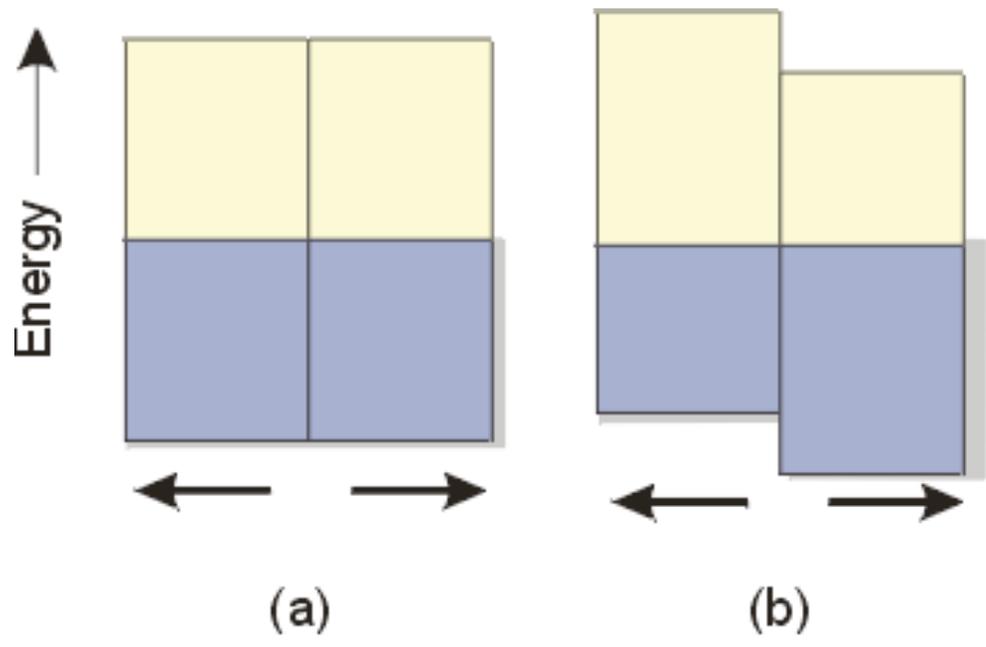




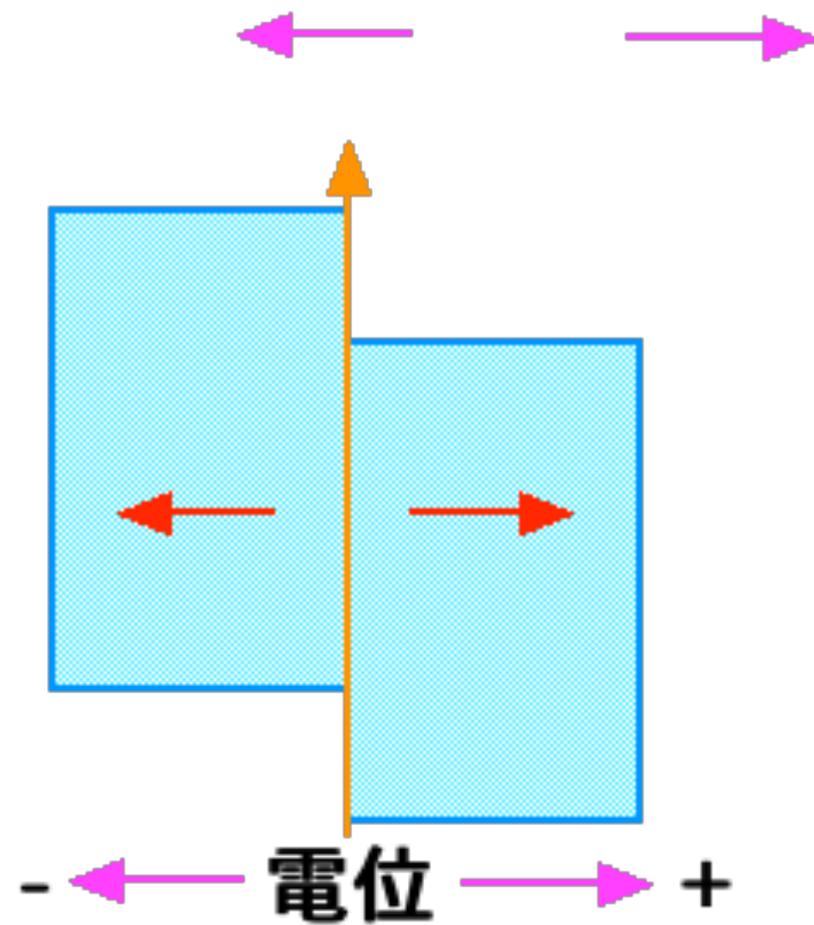


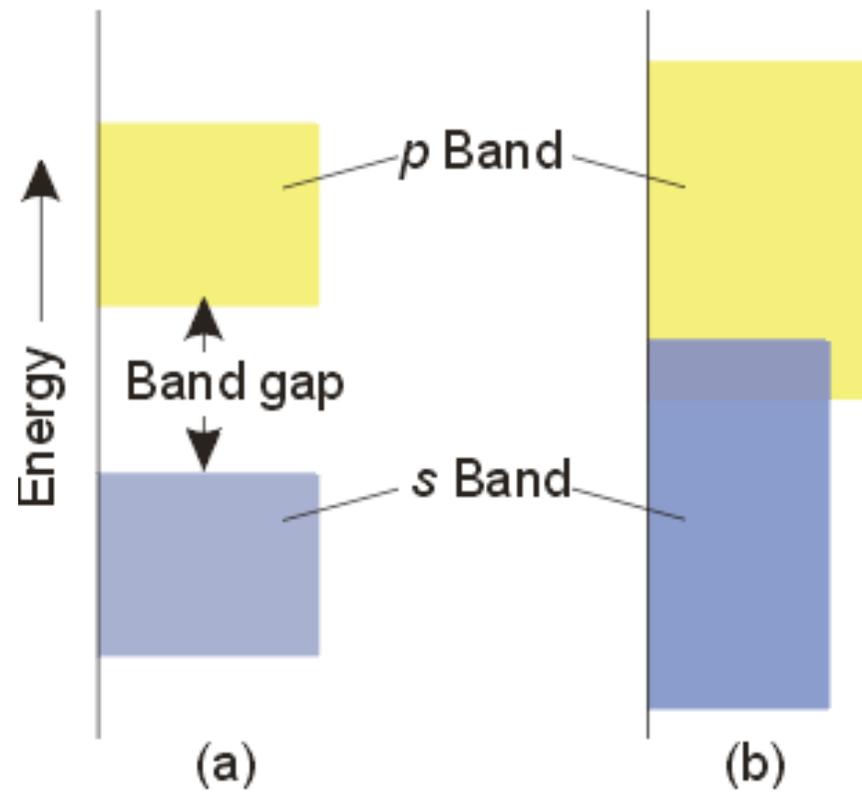
# (1) 金属の場合

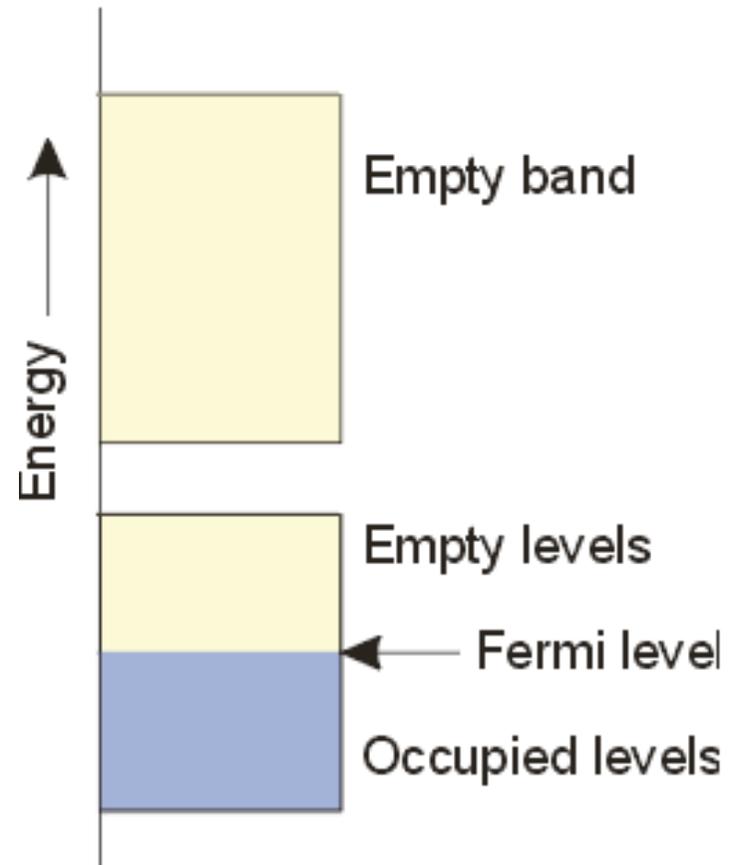


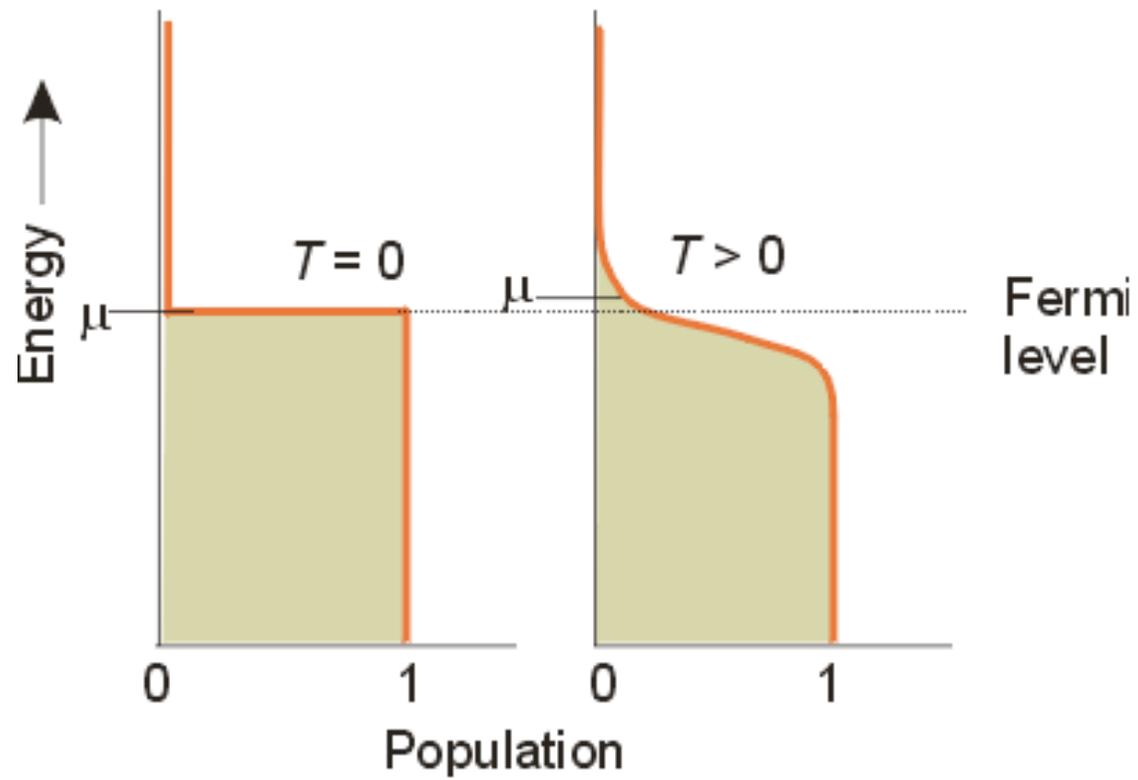


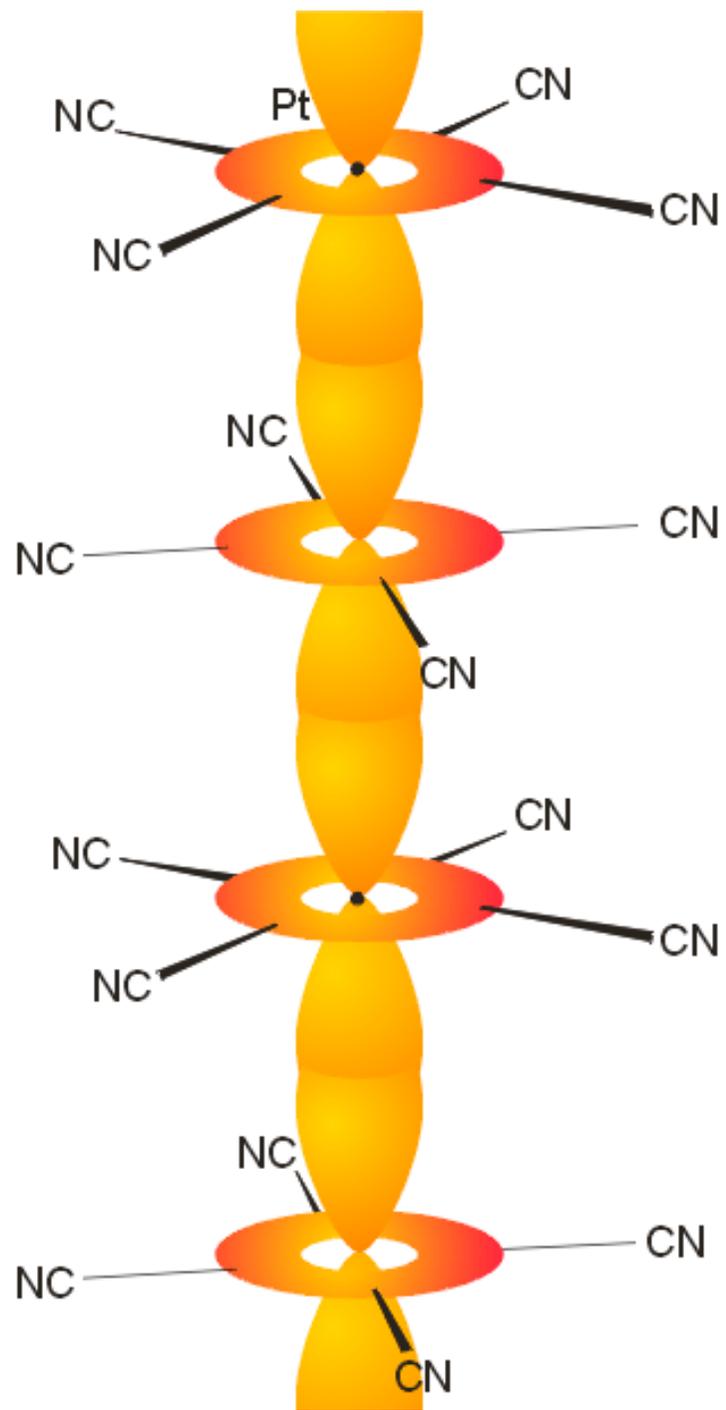
## (2)絶縁体の場合

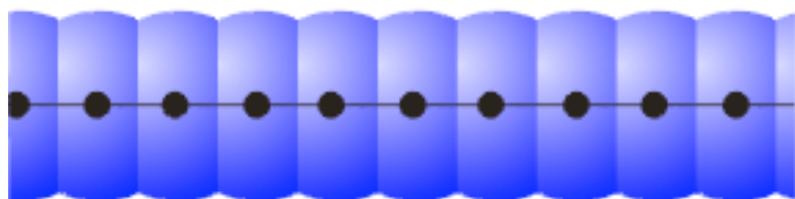




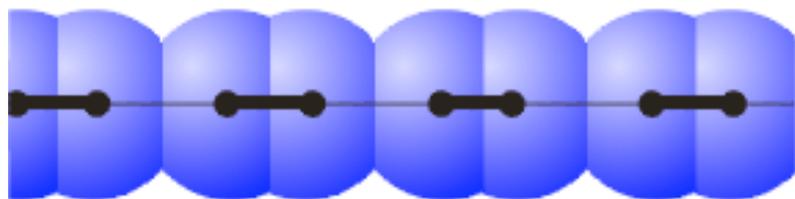




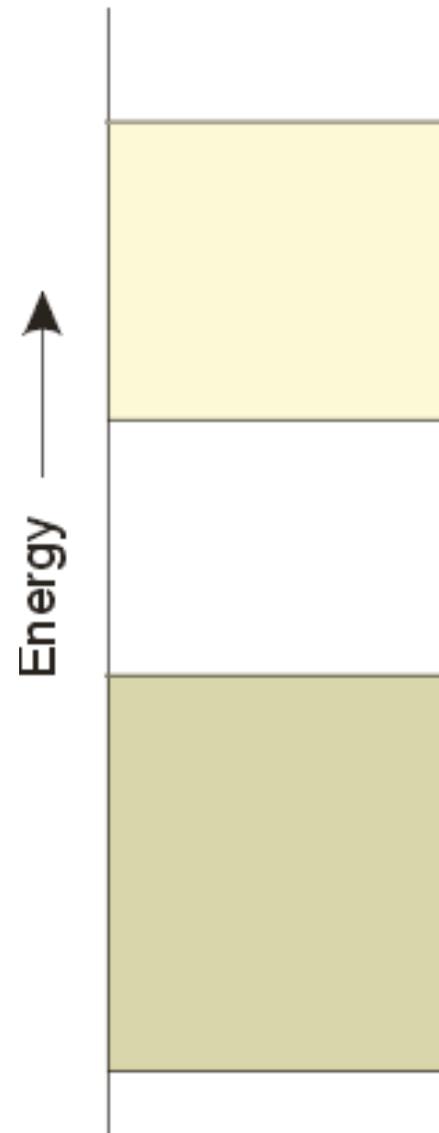


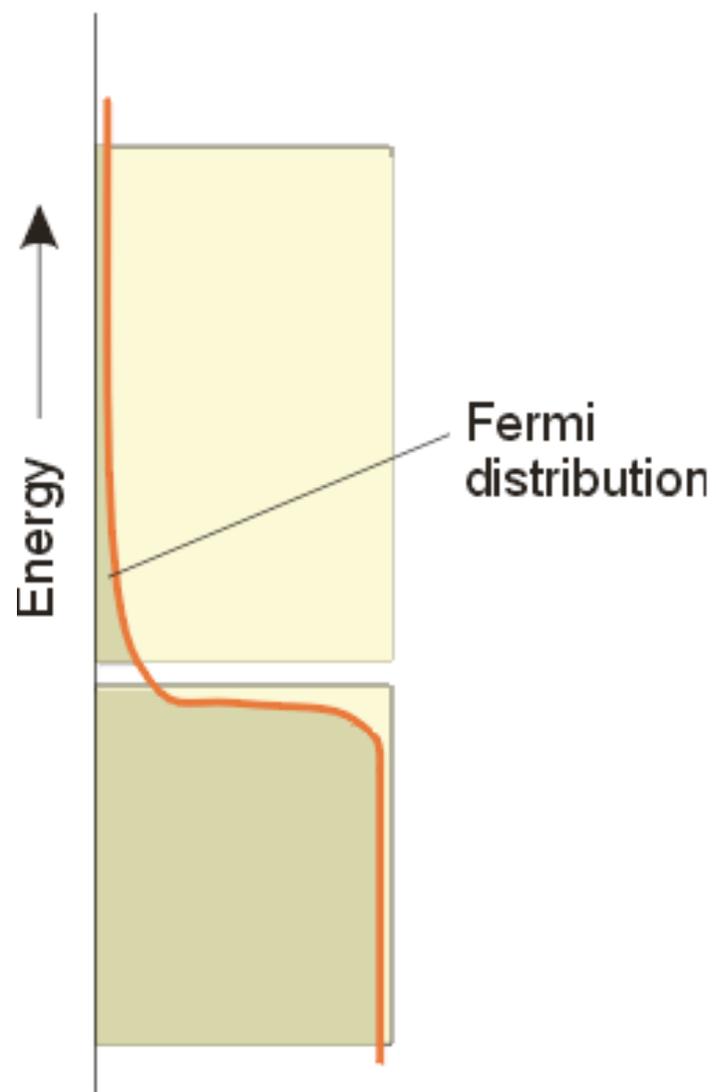


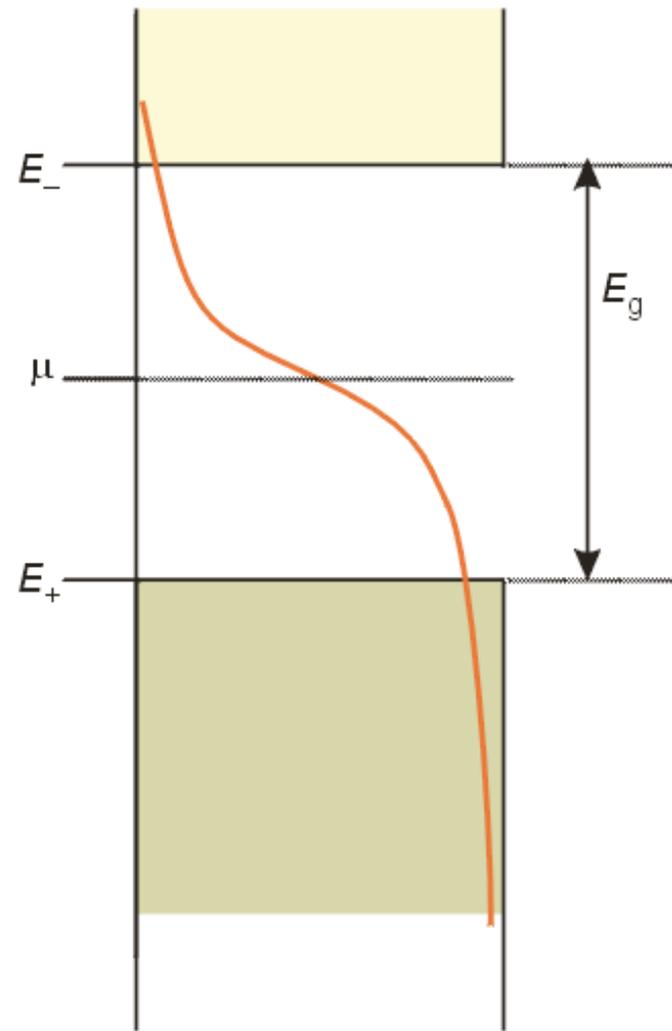
(a)

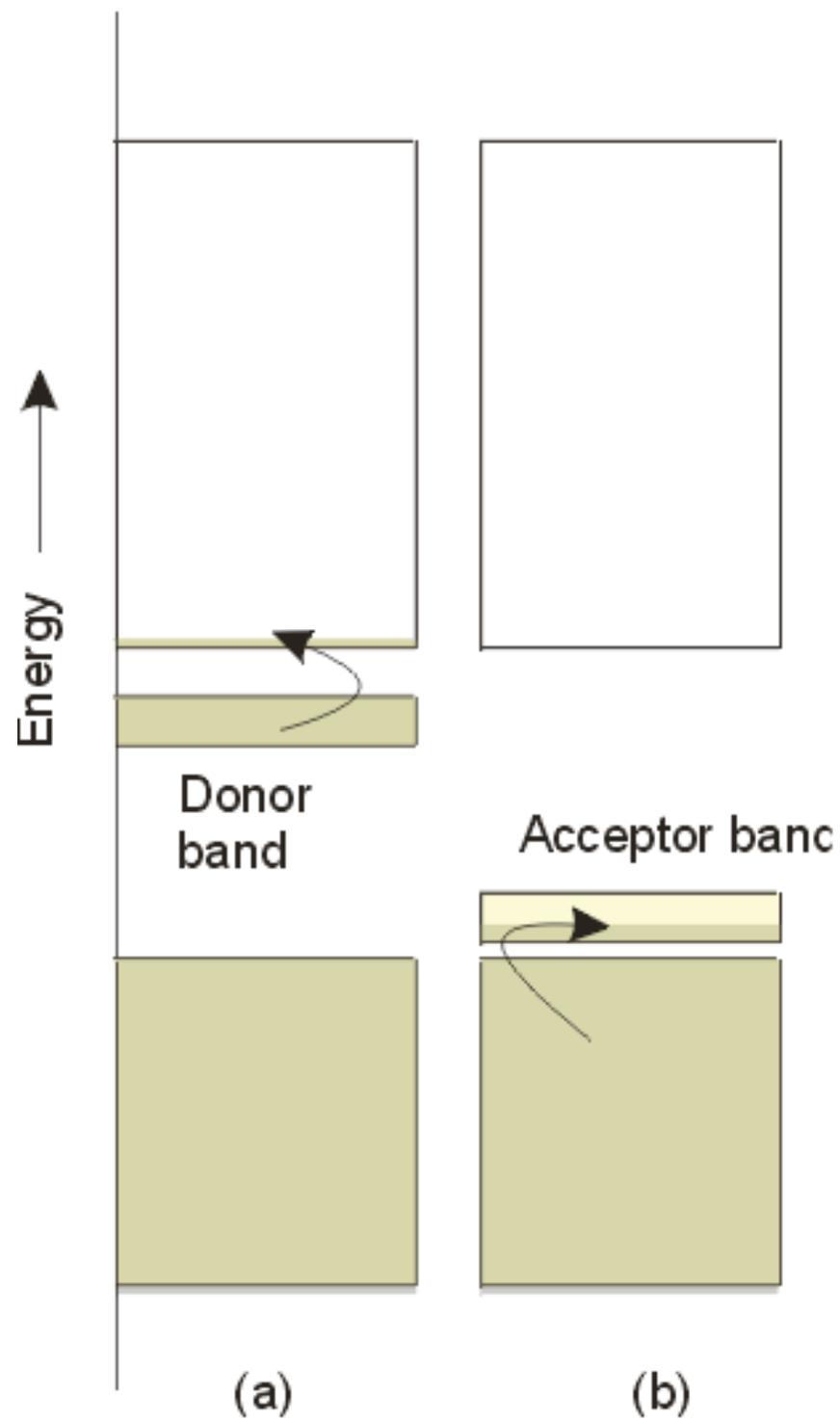


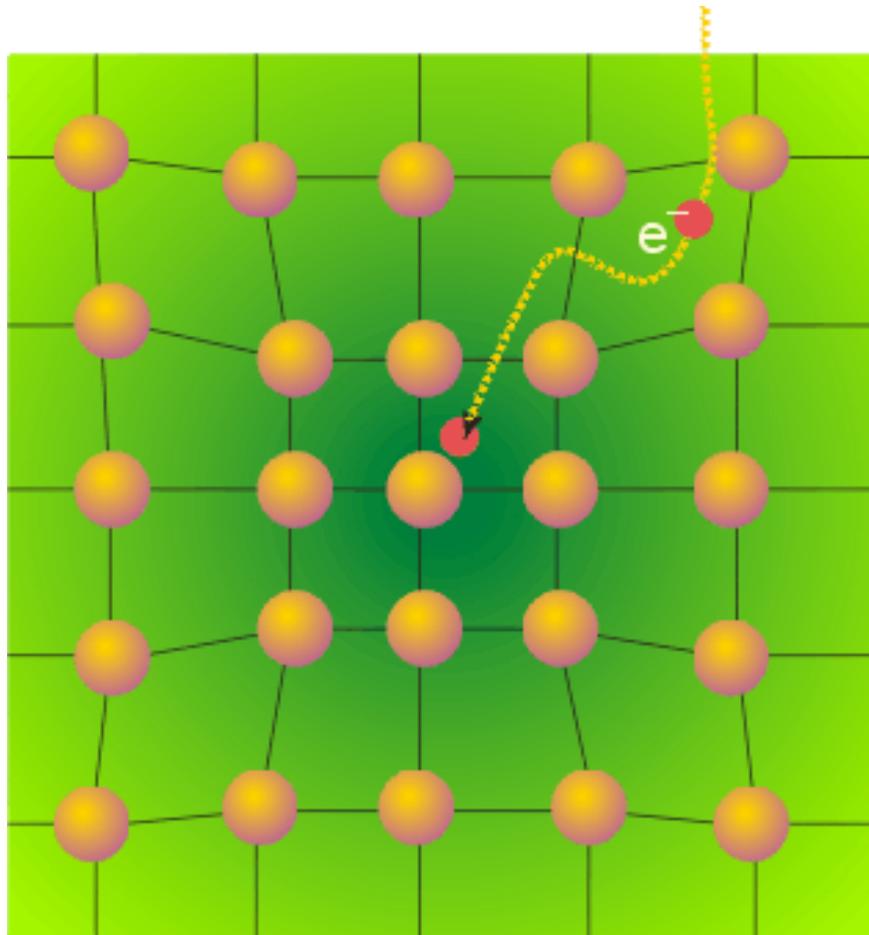
(b)



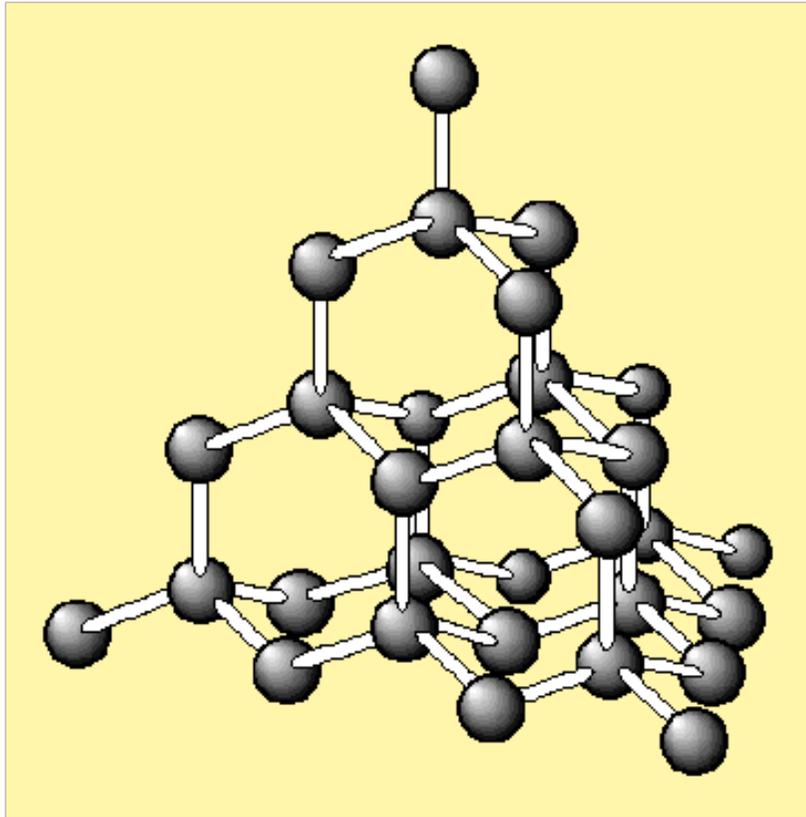




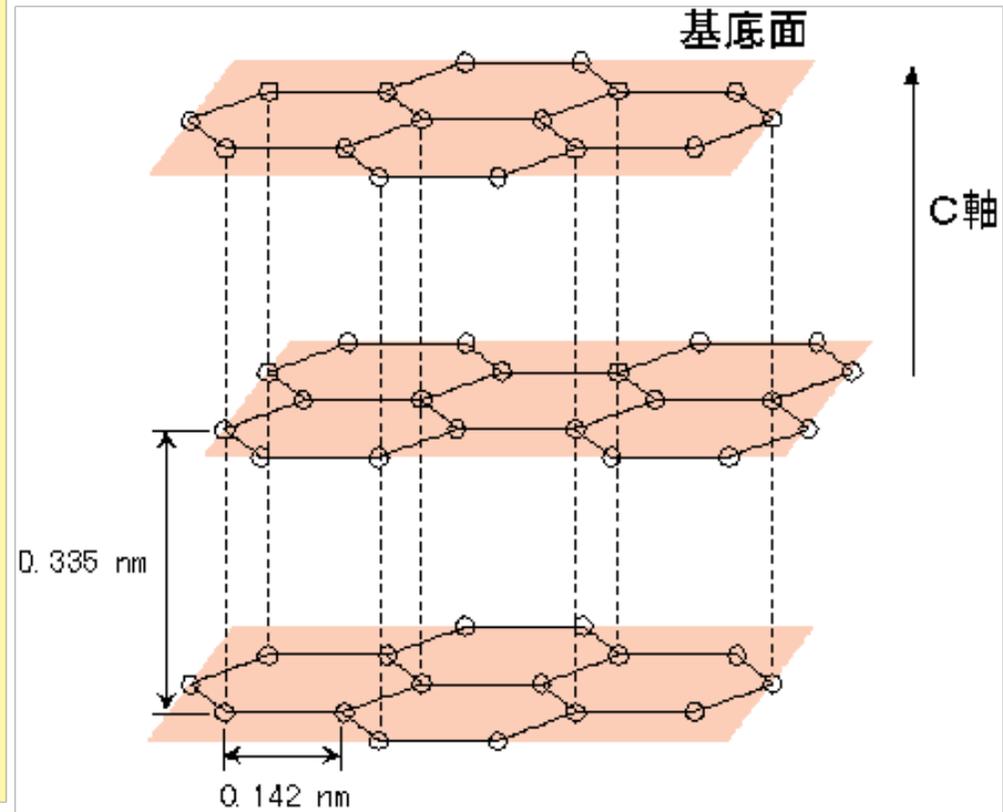




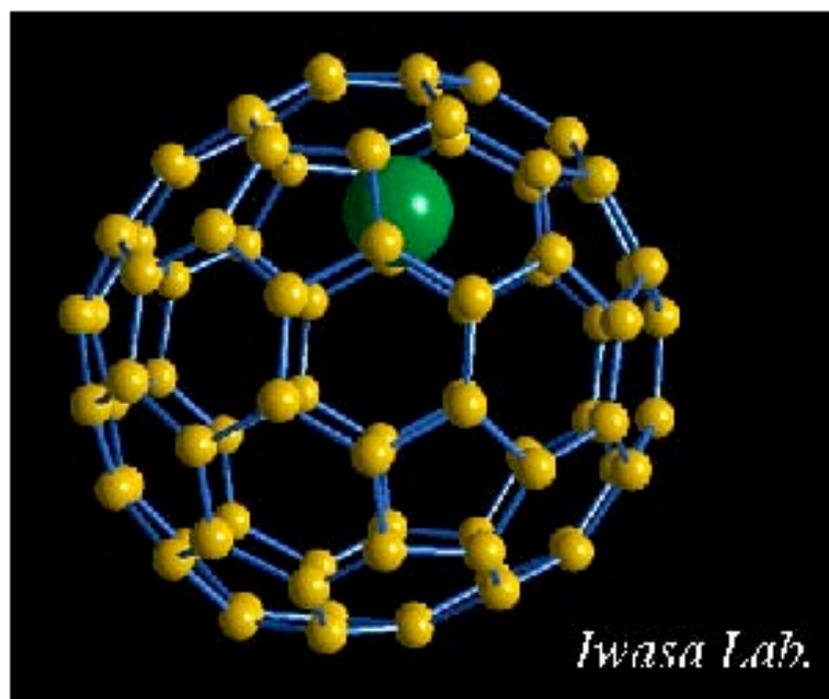
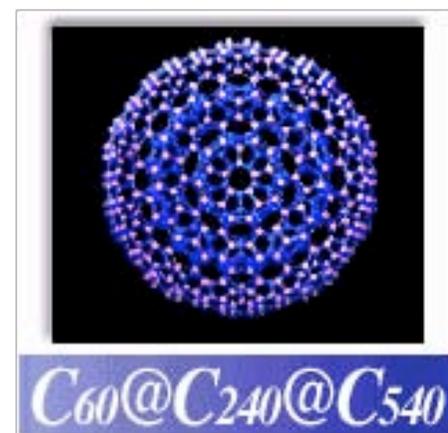
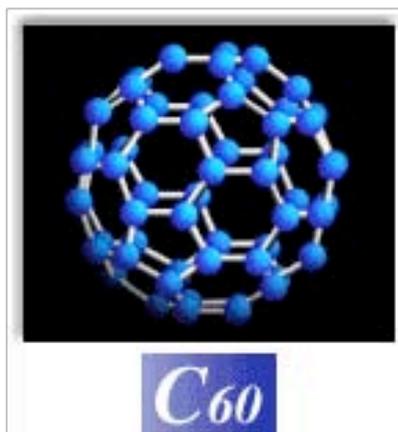
# 炭素

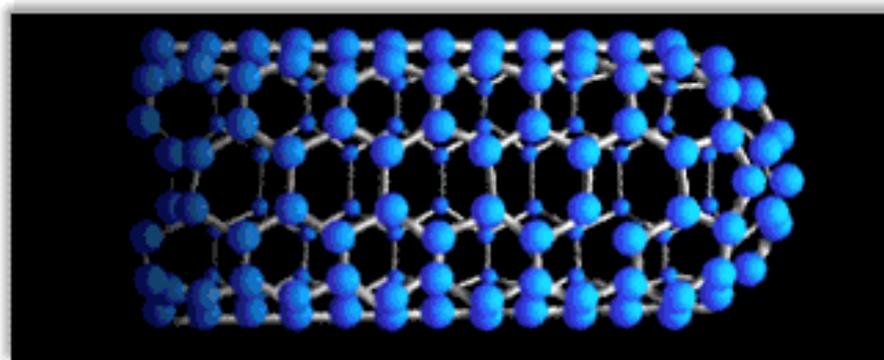
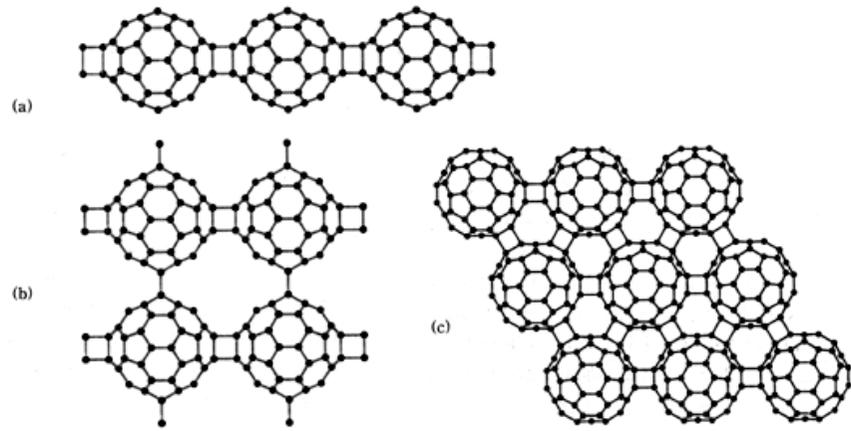


ダイヤモンド



グラファイト





*Nanotube*

電子供与体（ドナー）と  
電子受容体（アクセプター）

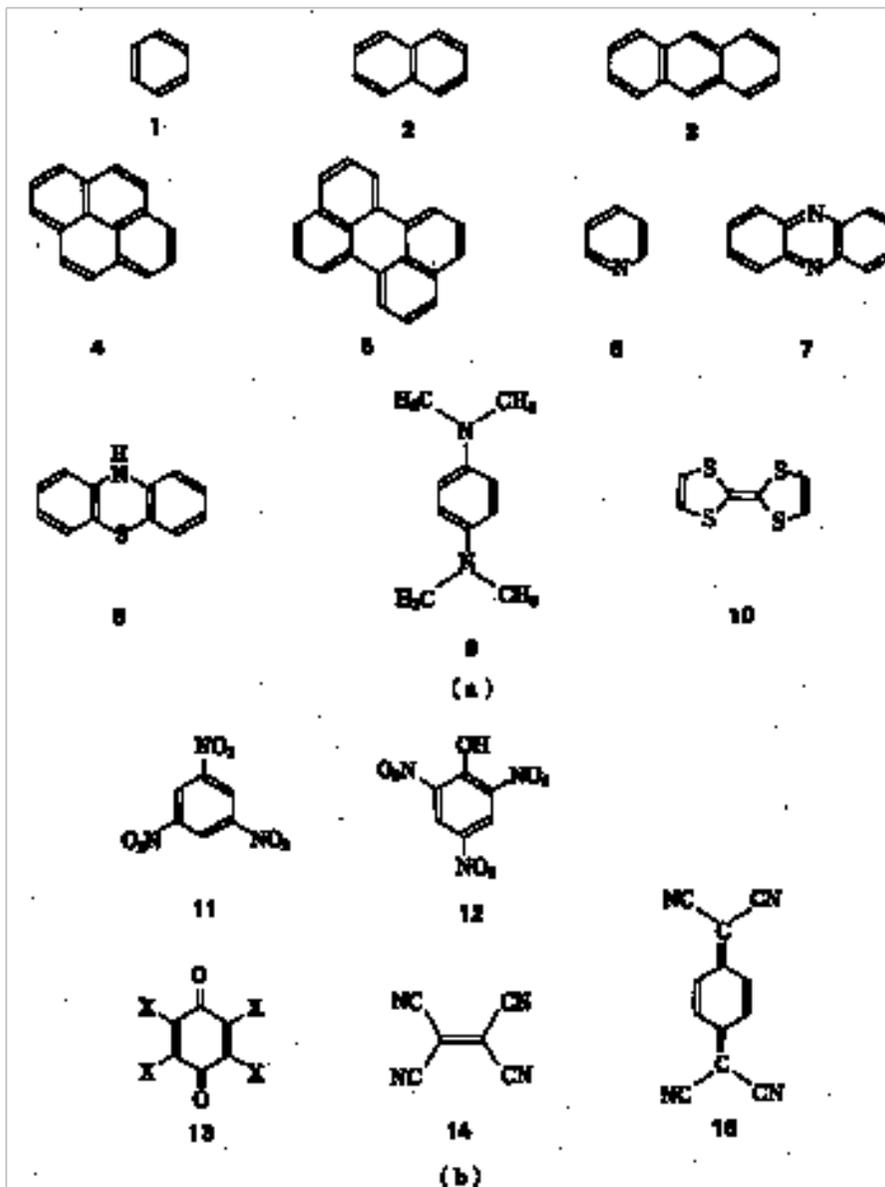
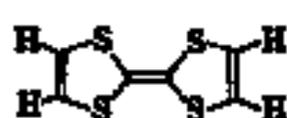


図 3. 4 (a) 電子供与体(ドナー)になりやすい分子  
 1 ベンゼン 2 ナフタレン 3 アントラセン 4 ペリレン  
 5 フェナントレン 6 ピリジン 7 フェナジン 8 フェノチアジン  
 9 *N,N,N',N'*-テトラメチル-*p*-フェニレンジアミン (TMPD)  
 10 テトラチアフルベレン (TTF)  
 (b) 電子受容体(アクセプター)になりやすい分子  
 11 1, 3, 5-トリニトロベンゼン 12 ピクリン酸  
 13 X=Cl: クロロオキノン, X=F: フルオロオキノン  
 14 テトラシアノエチレン (TCNE)  
 15 7, 7, 8, 8-テトラシアノキノジメタン (TCNQ)

表 5.1. 分子性金属, 超伝導体開発の展開

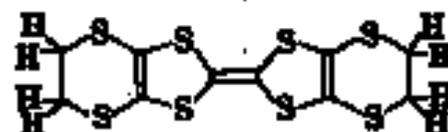
1968	$K_2Pt(CN)_4Br_{0.9} \cdot 3H_2O$ (KCP) 中心金属 (Pt) の $5d_{5/2}$ での金属-金属結合と電気伝導
1973	TTF-TCNQ 一次元金属 (カラム構造) バイエルス不安定性と電荷密度波 (CDW)
1980	$(TMTSF)_2X$ 有機超伝導体の出現 スピン密度波 (SDW)
1984	$\beta$ -(BEDT-TTF) $_2I_3$ 低- $T_c$ (1.5 K)
1985	$\beta$ -(BEDT-TTF) $_2I_3$ 高- $T_c$ (8 K)
1986	$\beta$ -(BEDT-TTF) $_2I_3$ わが国初の有機超伝導体 (TTF) $[Ni(dmit)_2]_2$ 初めての遷移金属錯体分子を含む超伝導体
1987	$(M_aN)[Ni(dmit)_2]_2$ $\pi$ アクセプター分子のみが伝導に参与する超伝導体 $\kappa$ -(BEDT-TTF) $_2Cu$ 層状超伝導体 $\pi$ 置分子配列 (DMET) $_2X$ 非対称的ドナーをもつ一連の超伝導体 $(R_1, R_2-DCNQI)_2Cu$ 配位構造をもつ分子性超伝導体
1988	$\kappa$ -(BEDT-TTF) $_2Cu(NCS)_2$ $T_c$ が 13K を越える
1990	$\alpha, \alpha'$ -TTF $[Pd(dmit)_2]_2$ Pd $[dmit]_2$ 超伝導体 $\kappa$ -(BEDT-TTF) $_2Cu[N(CN)_2]X$ , (X=Br, Cl) $T_c$ が 13K に上昇



TTF



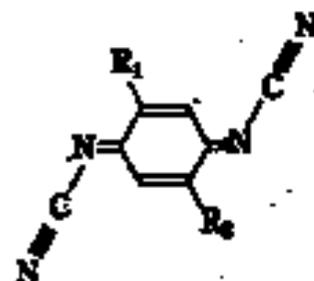
TMTSF



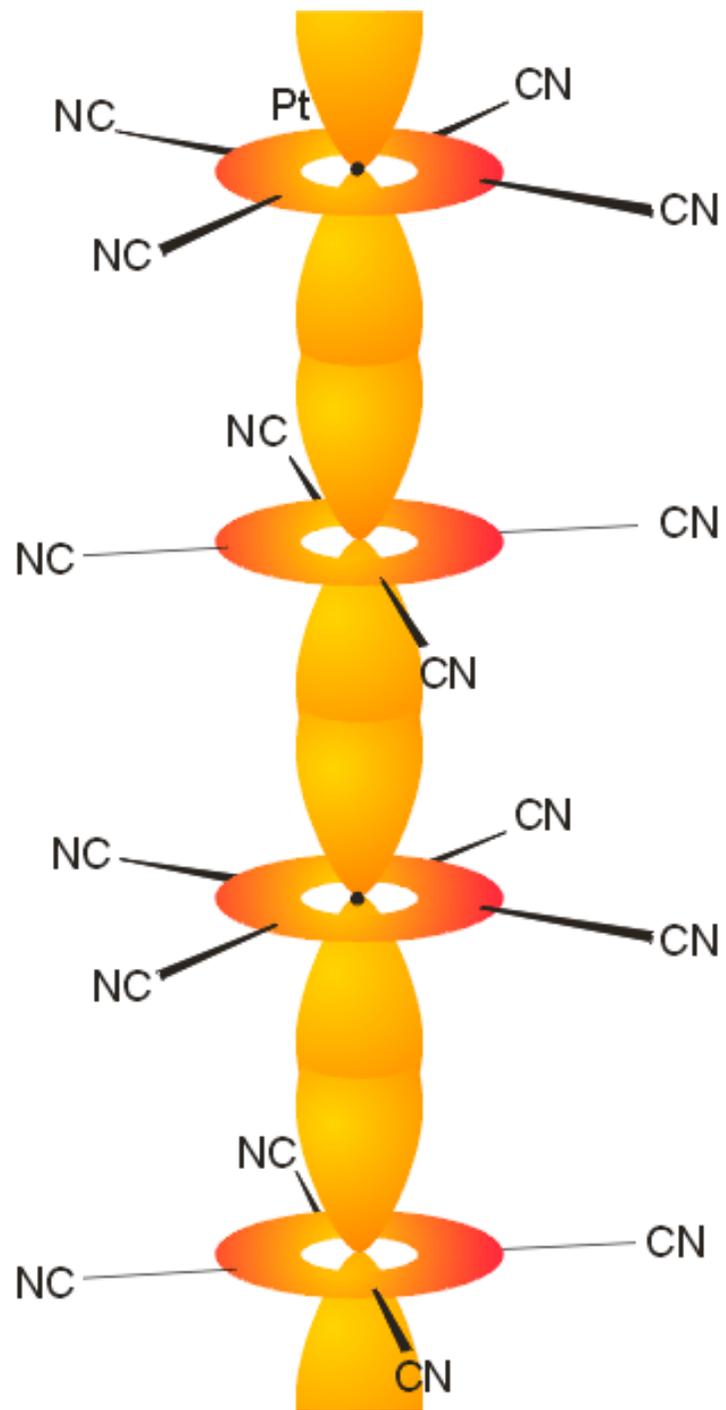
BEDT-TTF, ETとも略称される。



M(dmit) $_2$



$R_1R_2-DCNQI$





■ 1.6 (TMTSF)<sub>2</sub>X (X = PF<sub>6</sub>, ClO<sub>4</sub>...) の構造とフェルミ面。破線はフロンデルロー  
ルス面以下の 5p<sub>x</sub>...<sub>y</sub> 軌道

## 最初の有機超伝導体

# 国産初の有機超伝導体

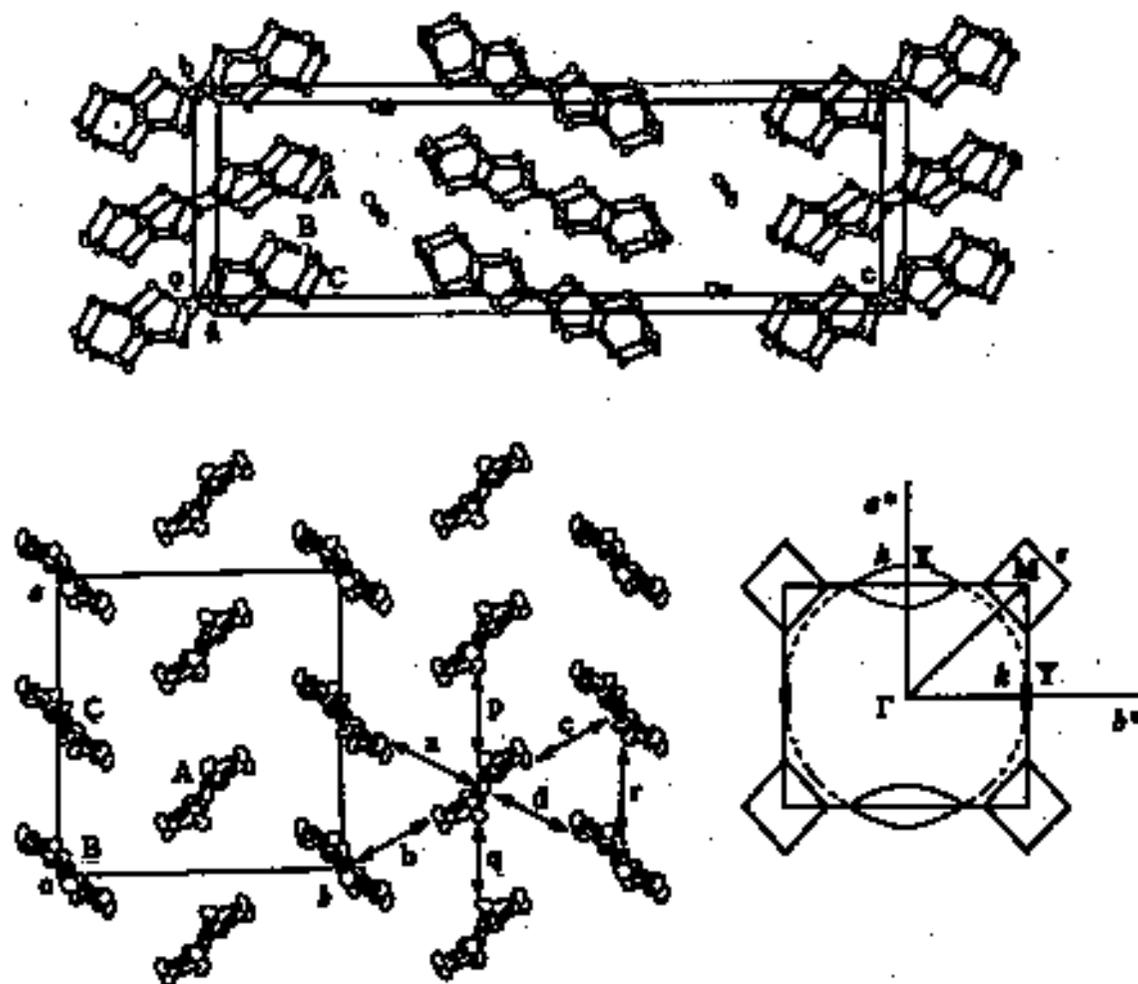


図 3.4  $\rho$ -(BEDT-TTF) $_2$ の結晶構造。金属層内分子配列および平均構造とヒュッケル法にもとづくフェルミ面。A, B, Cは独立な分子, a, bなどは独立な分子間相互作用をあらわす。破線は平均化された相互作用についての近似的な円筒フェルミ面の断面(図3.3参照)。Y近傍に小さなホール(h)領域が存在すること以外は実験結果とよくあっている。

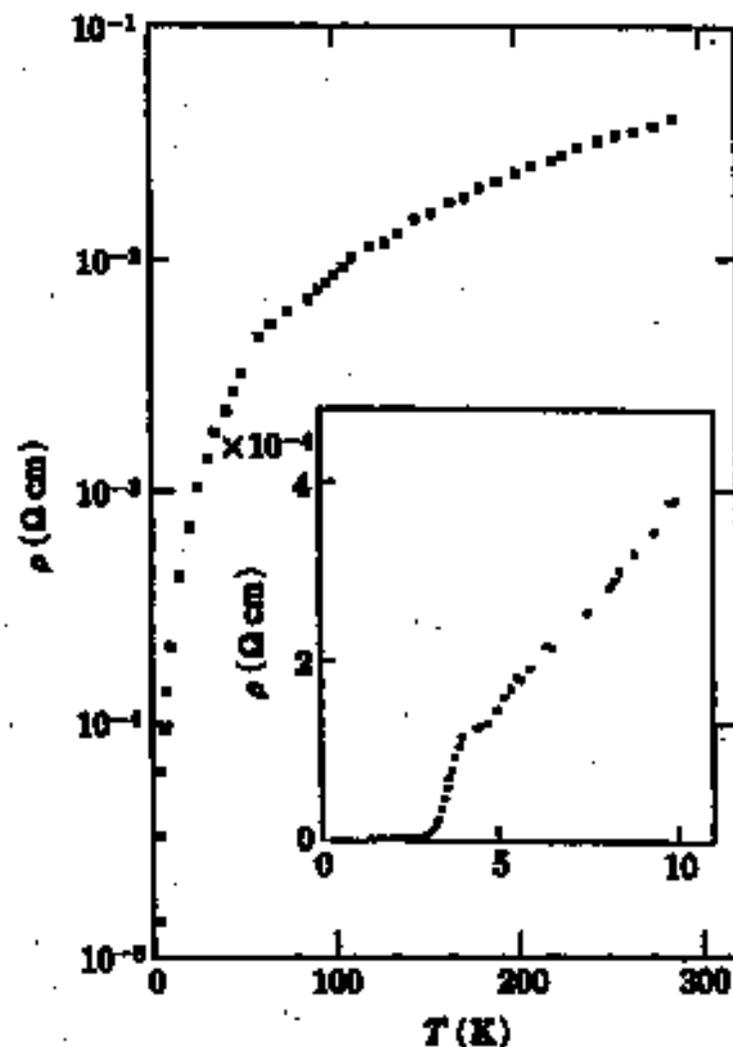
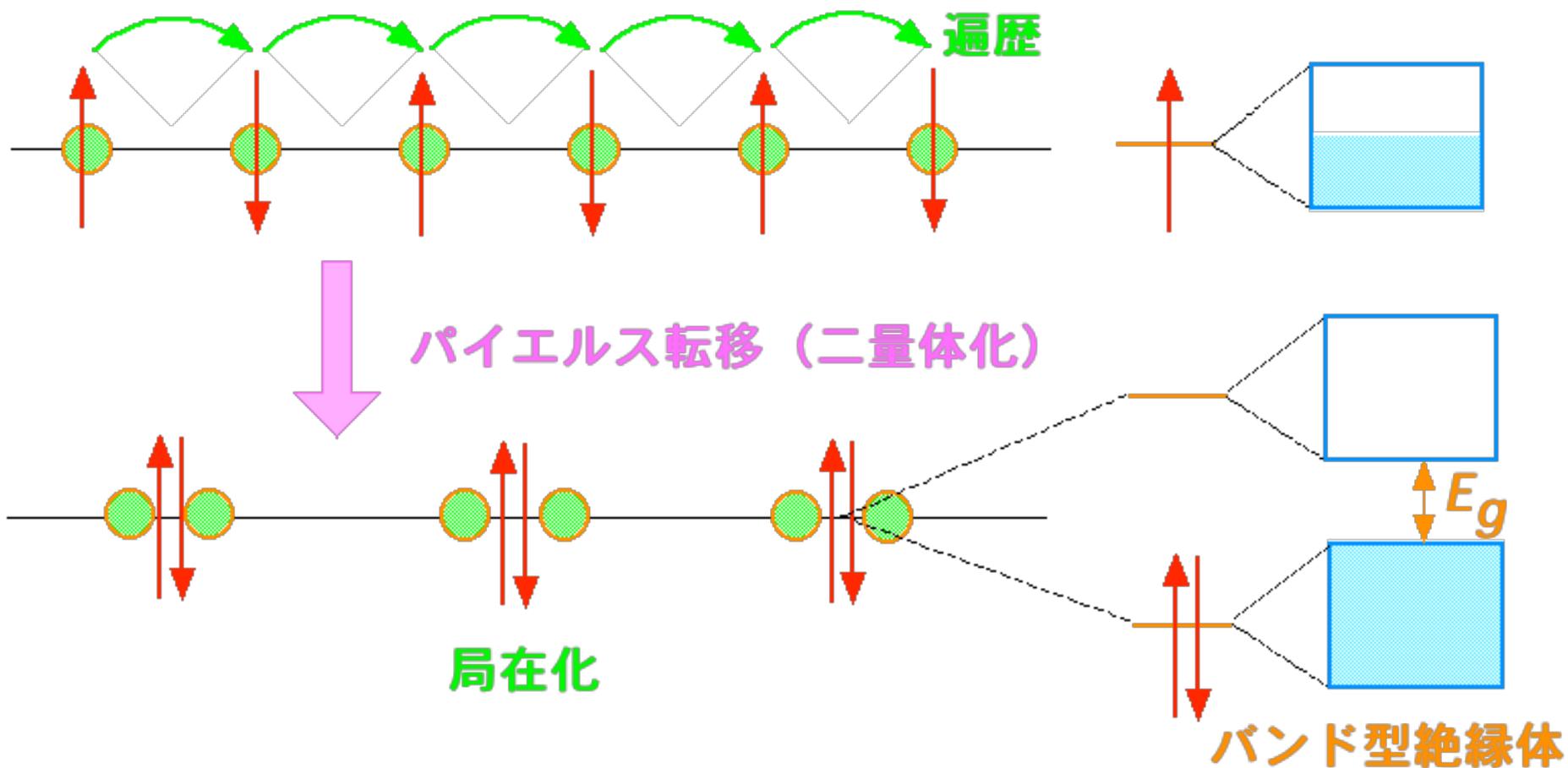


図 3.5  $\rho$ -(BEDT-TTF) $_2$ の超伝導転移。[Chem. Lett., 1988, 791.]

# 金属-絶縁体転移：M-I転移

## (1) パイエルス転移

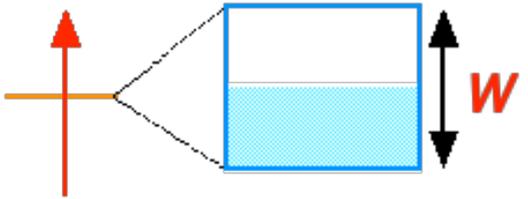
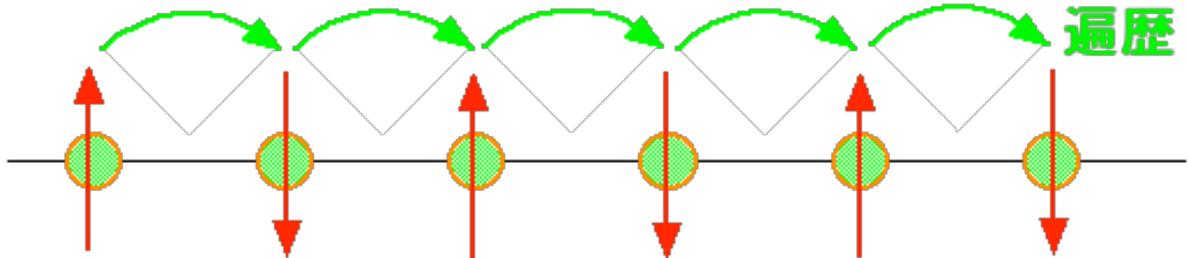
格子歪みに因る（電子-格子相互作用）



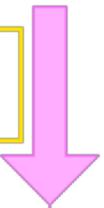
金属-絶縁体転移：M-I 転移

(2) モット転移

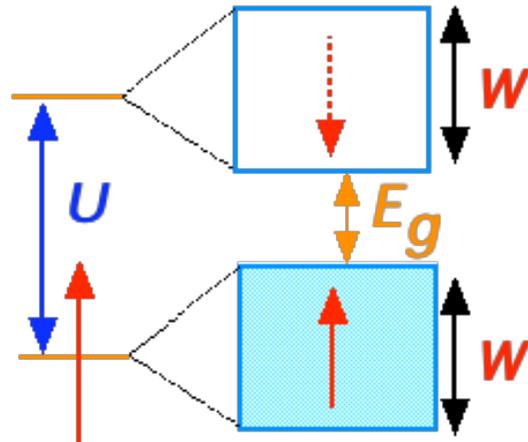
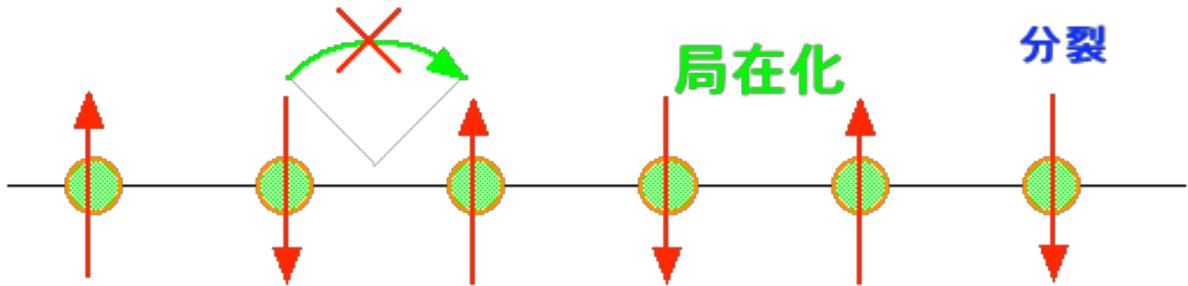
電子間反発  $U$  に因る (電子間相互作用)



$U > W$



モット転移 (格子歪無)



モット型絶縁体

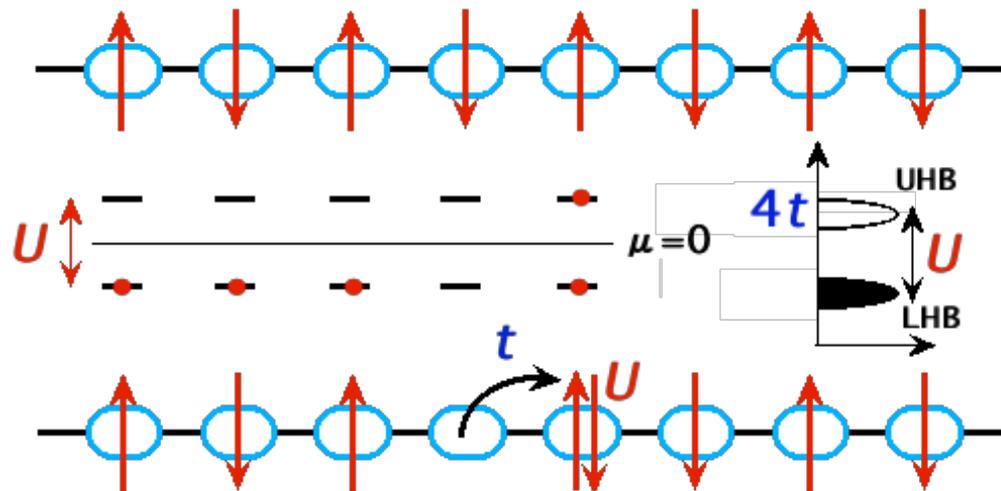
# Mott-Hubbard type insulator

ハバードモデル

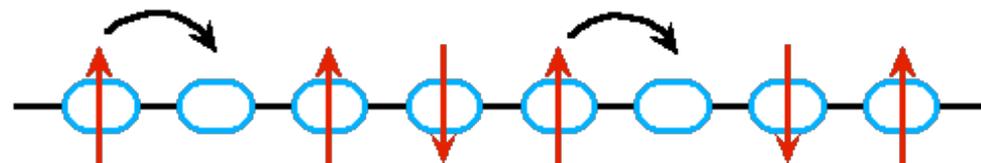
$$H = \sum_{i \neq j} t_{ij} c_{js} c_{is} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

移動積分 (波動性)      クーロン反発 (粒子性)

$N_e/N=1$  の場合 (半充填)      ○ 2人掛けの椅子



$N_e/N \neq 1$  の場合



$N_e/N=1$ の場合(半充填)

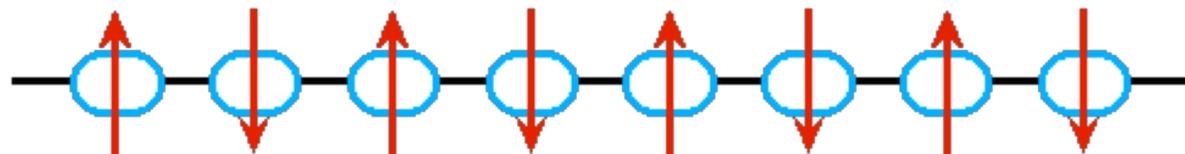
(1)  $U > W$  ( $\sim 4t$ ): モット絶縁体

Magnetic disorder

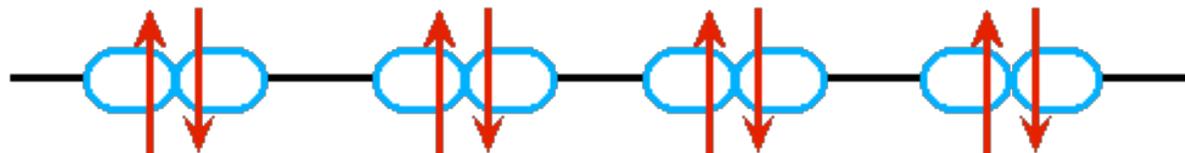


基底状態

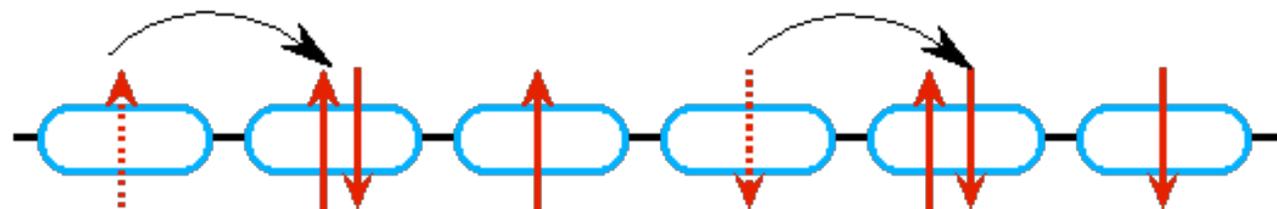
(a) SDW (鎖間相互作用大)



(b) Spin Peierls (鎖間相互作用小)

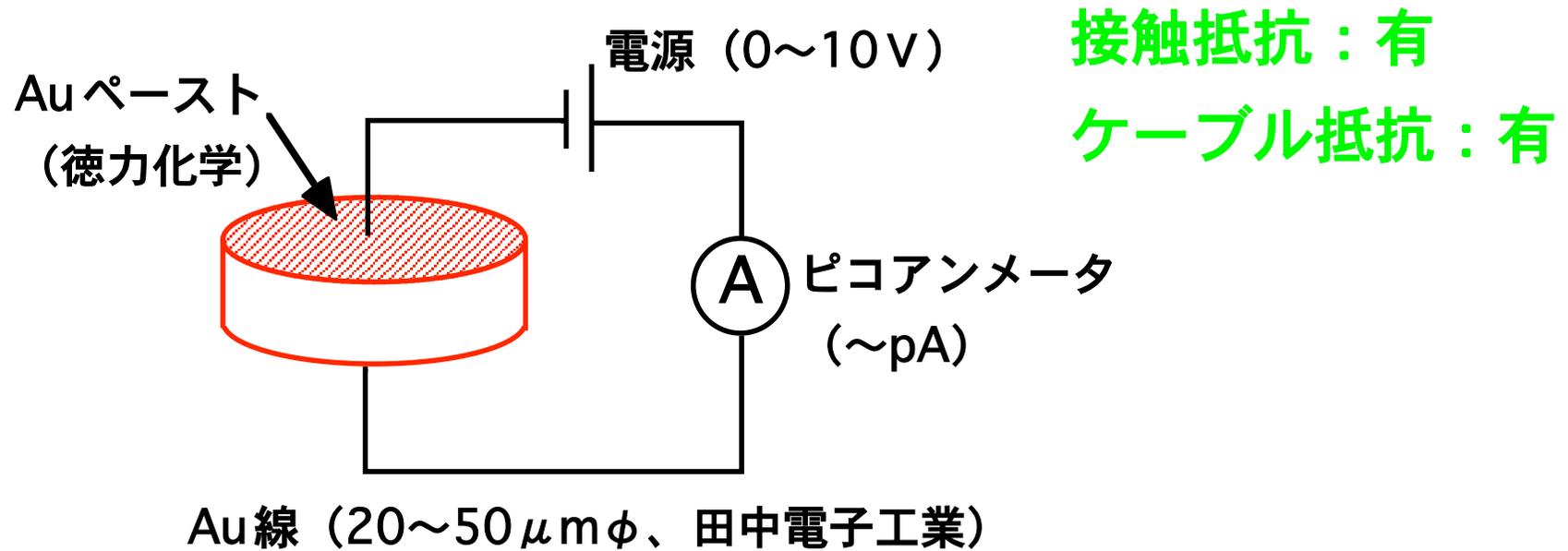


(2)  $U < W$  ( $\sim 4t$ ): 金属

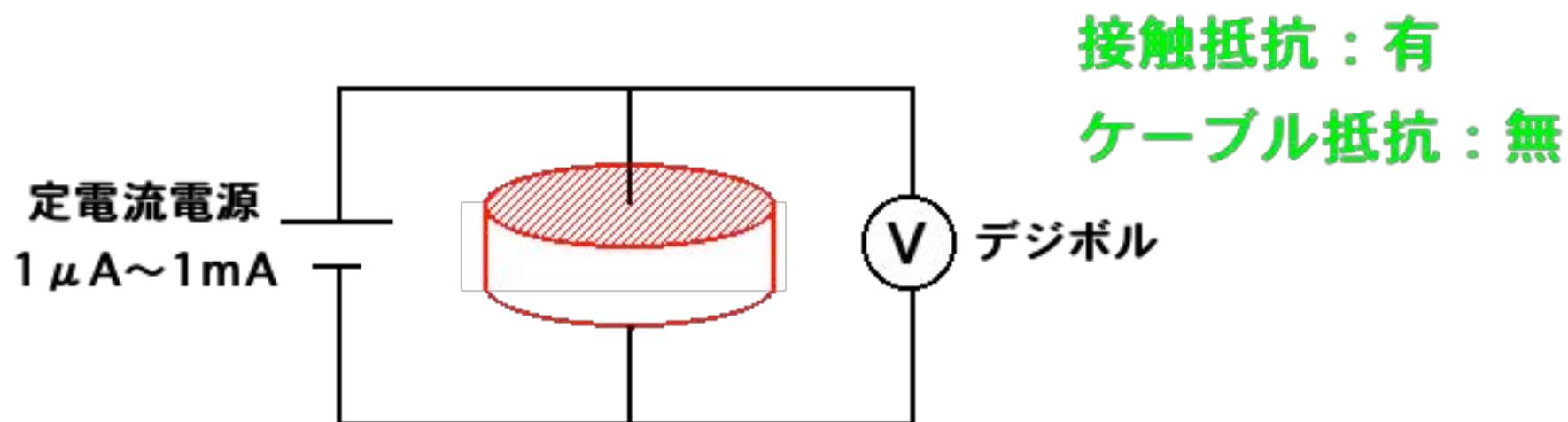


# 測定方法

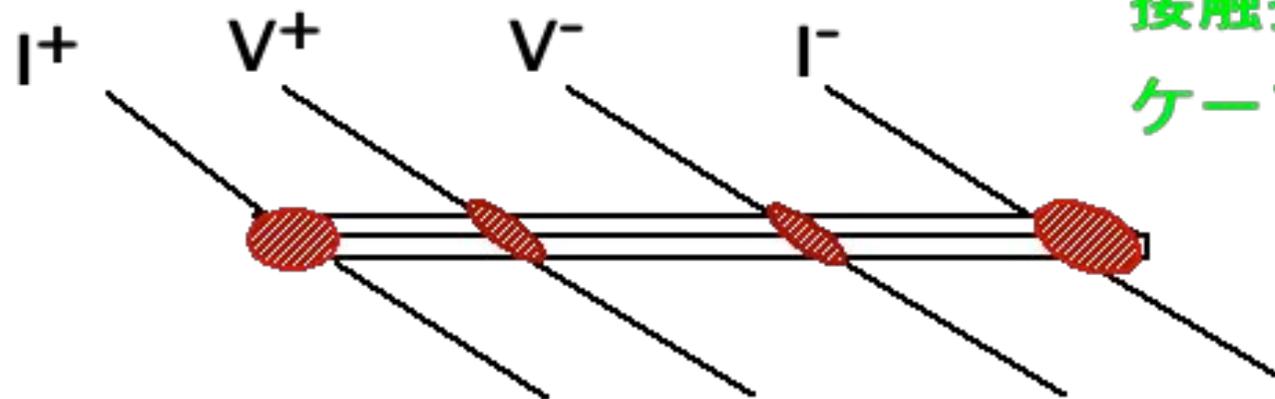
- 二端子法（高抵抗の場合、 $\rho > 10^8 \Omega \text{cm}$ ）



- ・ 擬似四端子法（粉末試料、 $\rho > 10^3 \Omega \text{cm}$ ）



- ・ 四端子法 (単結晶試料、 $\rho < 10^3 \Omega \text{cm}$ )



接触抵抗：無

ケーブル抵抗：無

# 金属伝導性錯体を創るには

## 1. 集積系であること

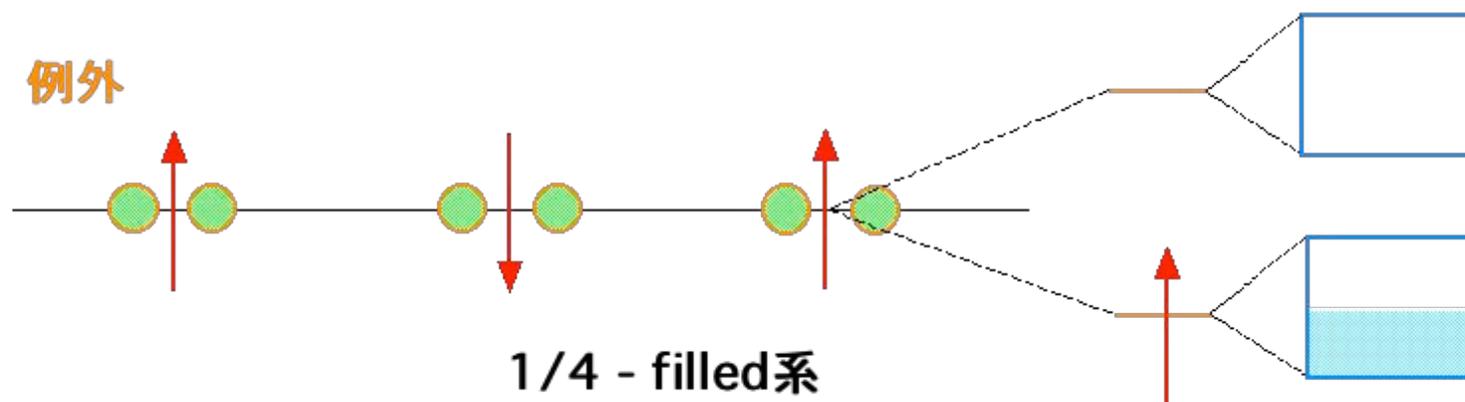
- ・ ディスクリート系では無理
- ・ 架橋配位子を用いる（共有結合ネットワーク）
  - 架橋イオン（ハロゲンイオン、酸素イオン、 $\pi$ 共役系）
- ・ 短い分子間距離（ファンデルワールスネットワーク）
  - M-M距離  $< 3.0 \text{ \AA}$ 、 $\pi$ - $\pi$ 距離  $< 3.4 \text{ \AA}$

## 2. 不対電子（ラジカル）を有する

- ・ 閉殻構造でない、部分酸化状態、混合原子価状態

## 3. ユニフォームな構造を有する

- ・ 超周期がない、二量体化していない、構造歪みがない。



# 金属伝導性錯体を創るには

## 4. 次元性をあげる

- ・パイエルス転移を抑制する

## 5. オンサイトクーロン反発 $U$ を減少させる

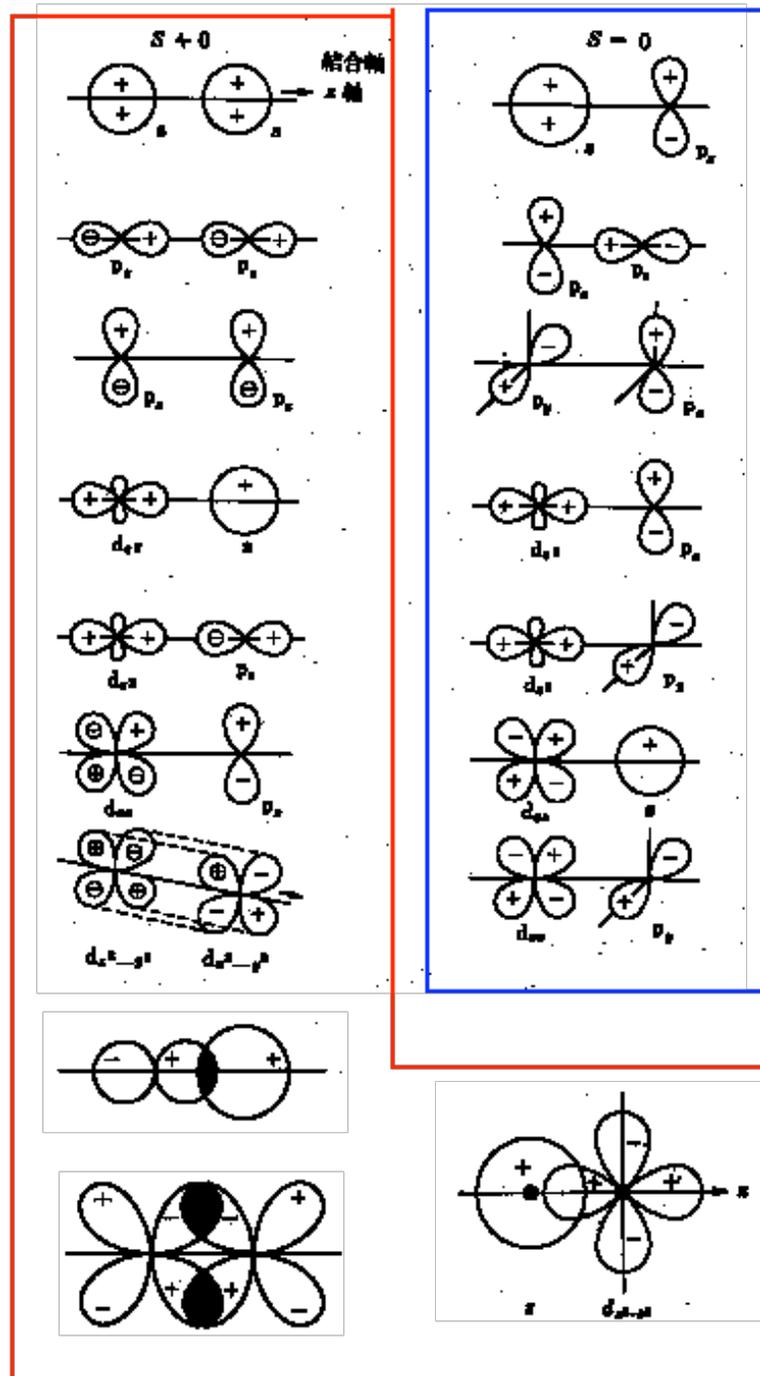
- ・電子雲拡大、大きい  $\pi$  共役系、金属間結合

## 6. フロントティア軌道工学

- ・結晶工学では駄目、軌道の対称性、直交性の考慮
- ・電荷移動型軌道工学（セルフ・ドーピング）
- ・架橋型軌道工学（ $\sigma$  型架橋、 $\pi$  型架橋）
- ・ダイレクト型軌道工学（外部ドーピング）

## 7. 努力（物質観）と運（動物的臭覚）

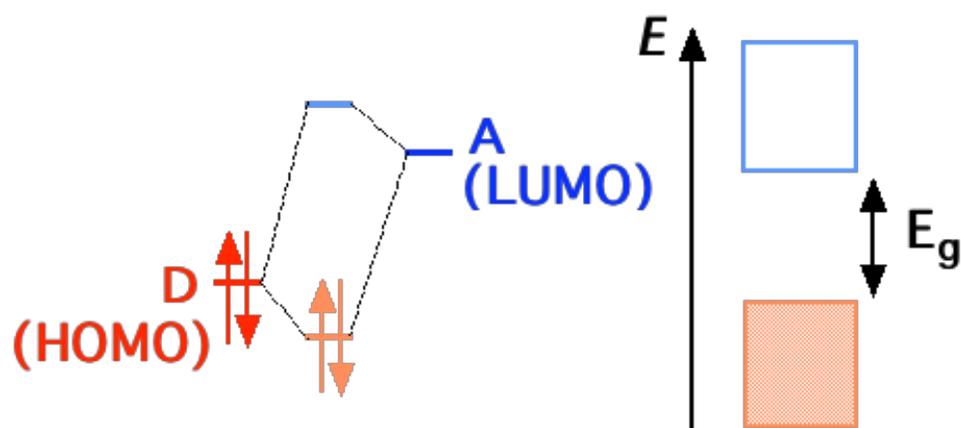
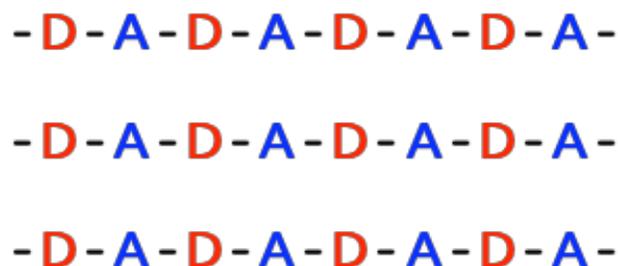
# 軌道の対称性、直交性、重なり積分



電荷移動型軌道工学  
(セルフ・ドーピング)

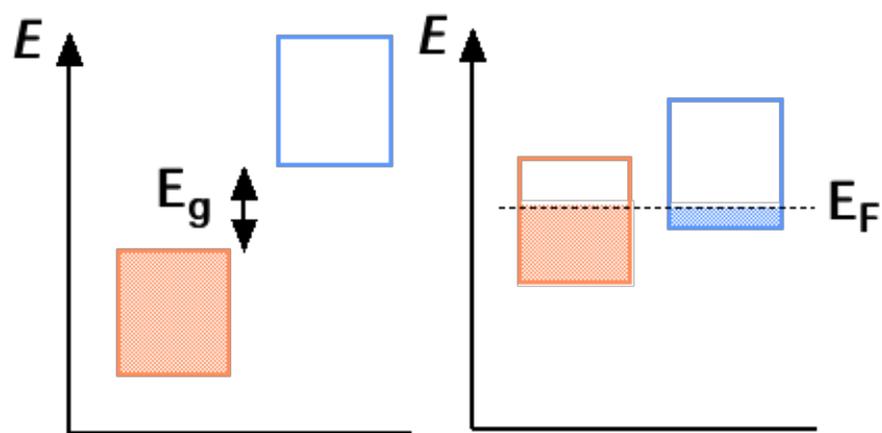
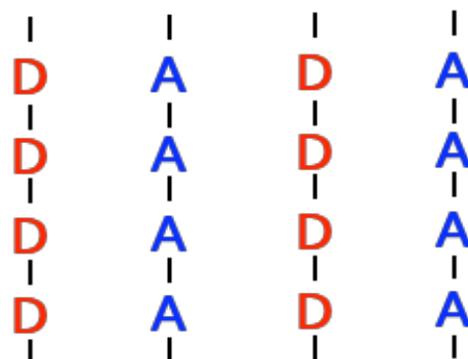
D : ドナー、A : アクセプター

(1) 交互積層型



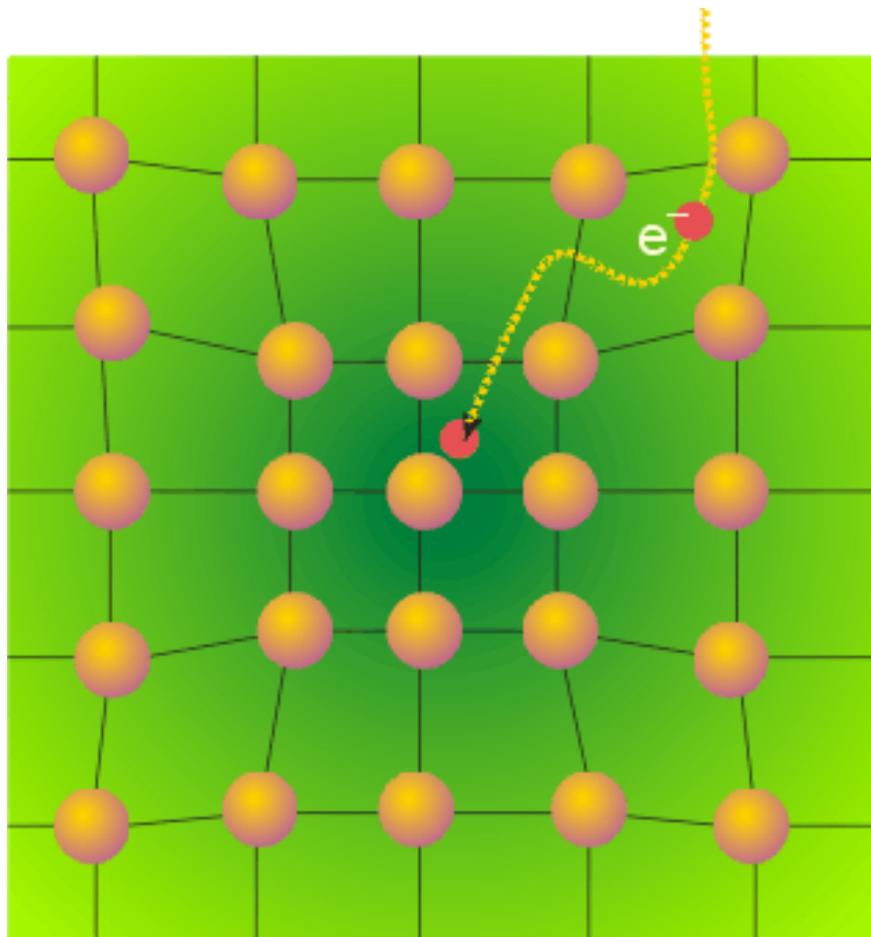
但し、強制ドーピングで金属化

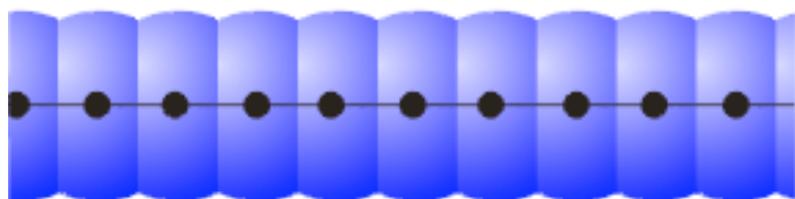
(2) 分離積層型 (セルフドーピング)



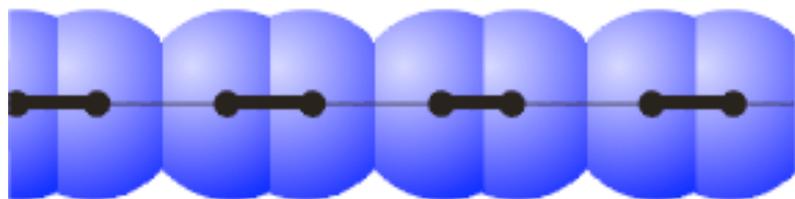
中性状態

電荷移動状態

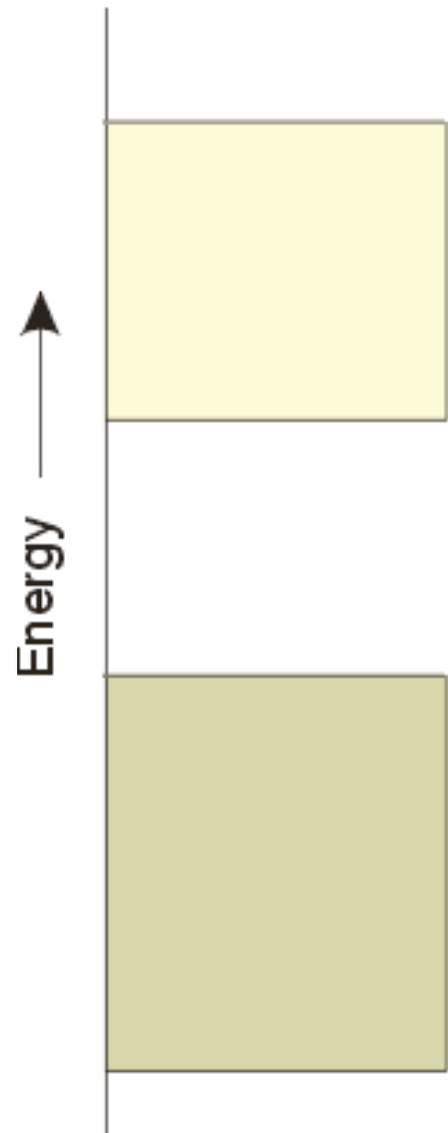




(a)



(b)



## 物質の磁化機構

$$M = \chi H$$

$$\chi = N \mu^2 / 3 k_B T$$

$$\mu^2 = g^2 J(J+1) \mu_B^2$$

$\mu_B$ : 電子の磁子 (磁気モーメントの量子力学的単位)  
 $9.274 \times 10^{-21}$  erg/G

$$\chi = C / T \quad C = 0.375 (S = 1/2)$$

g因子:  $\Delta E = g \mu_B H$

$k_B$ : ボルツマン定数 ( $1.38041 \times 10^{-16}$  erg/K)

常磁性(不対電子)

反磁性(電子対)

完全反磁性(クーパー対、マイスナー効果)

強磁性(キュリー温度)

反強磁性(ネール温度、磁気異方性)

フェリ磁性

反強磁性になる理由

電子雲の重なり効果

強磁性になる理由

フント則、ヒステリシス

超交換相互作用

90°パス、180°パス

二重交換相互作用

$\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}_3\text{O}_4$

スピントロスコオーバー錯体

金属の常磁性(パウリ常磁性)

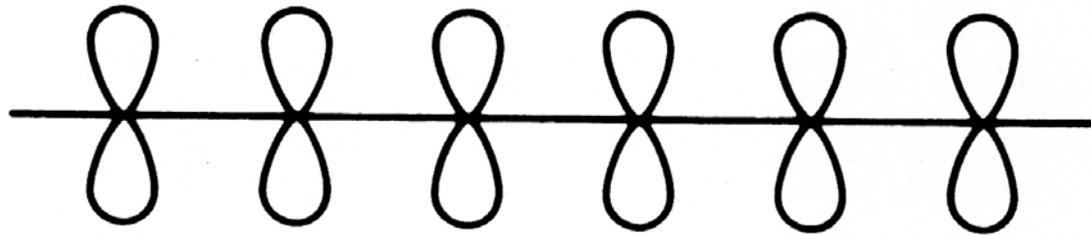
スピン数:  $2\mu_B HD(E_F)$

1モル磁化:  $2N\mu_B^2 HD(E_F)$

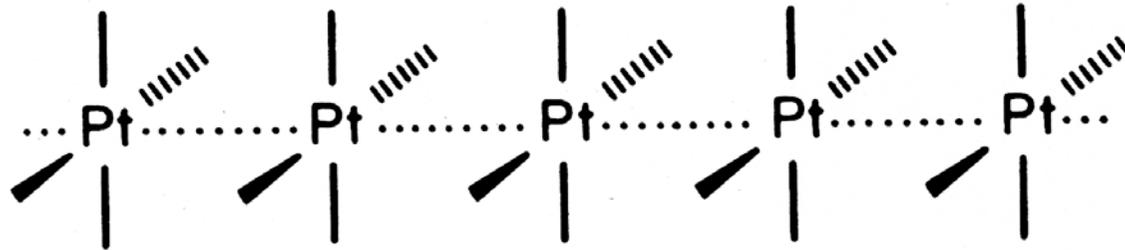
バンド強磁性: Ni

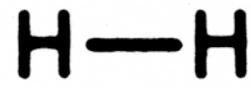
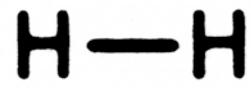


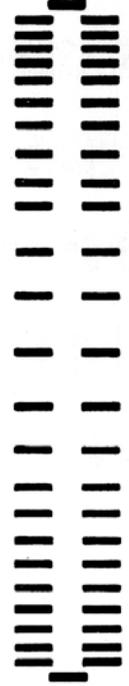
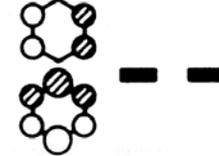
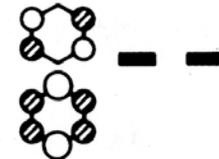
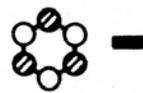
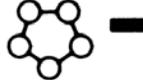
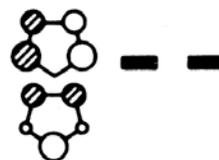
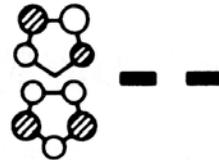
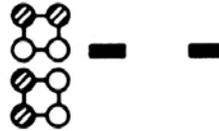
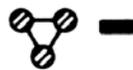
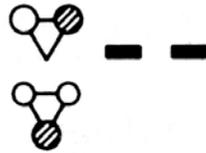
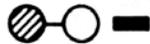
1

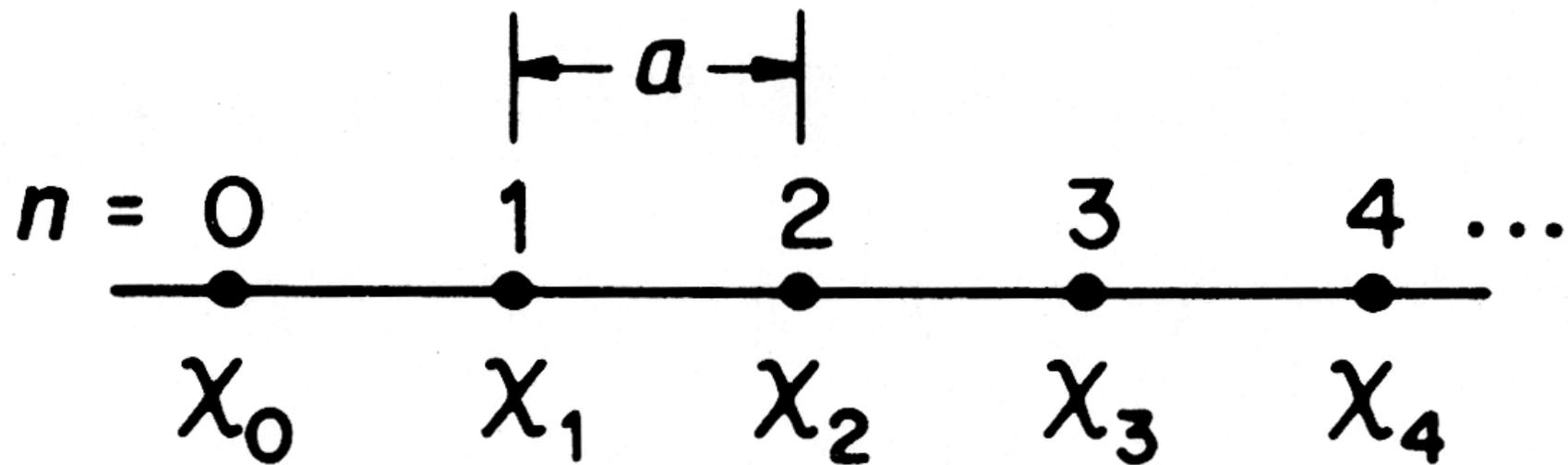


2









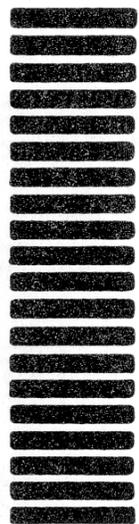
$$\psi_k = \sum_n e^{ikna} \chi_n$$

$$k=0 \quad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$$

$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$


$$k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n} \chi_n = \sum_n (-1)^n \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$

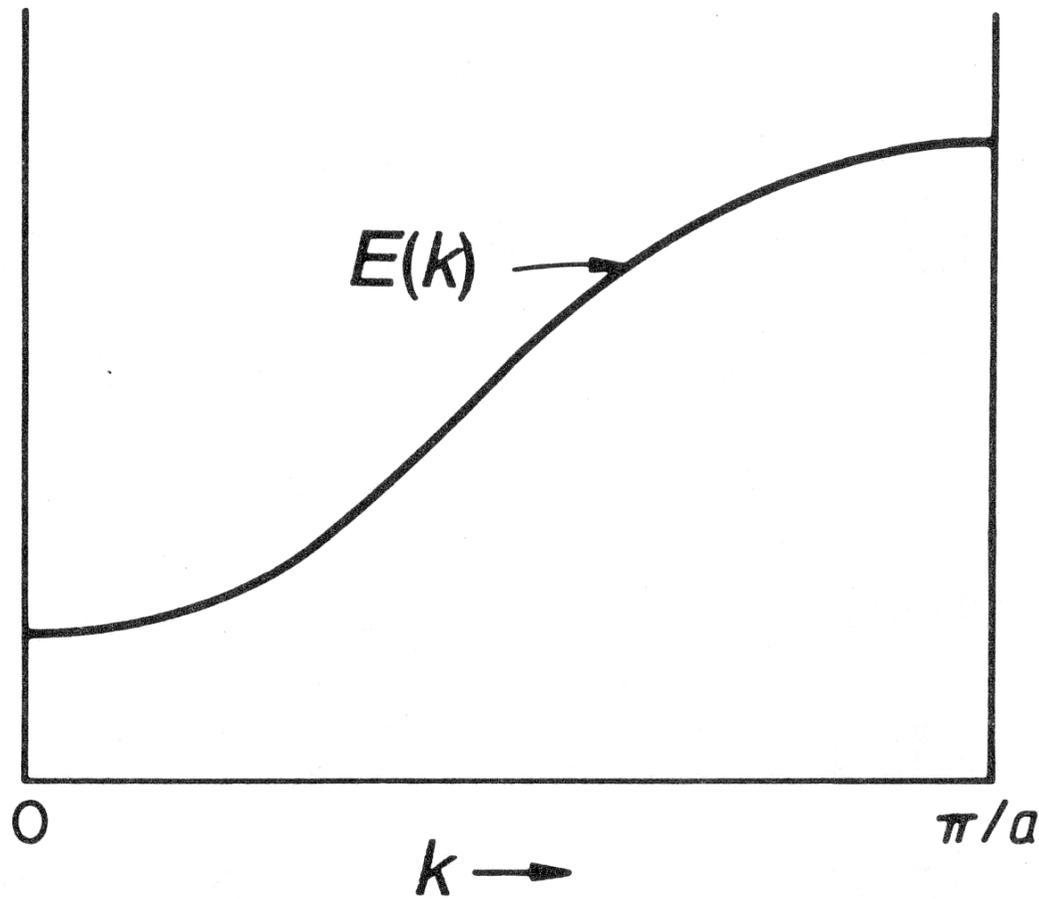



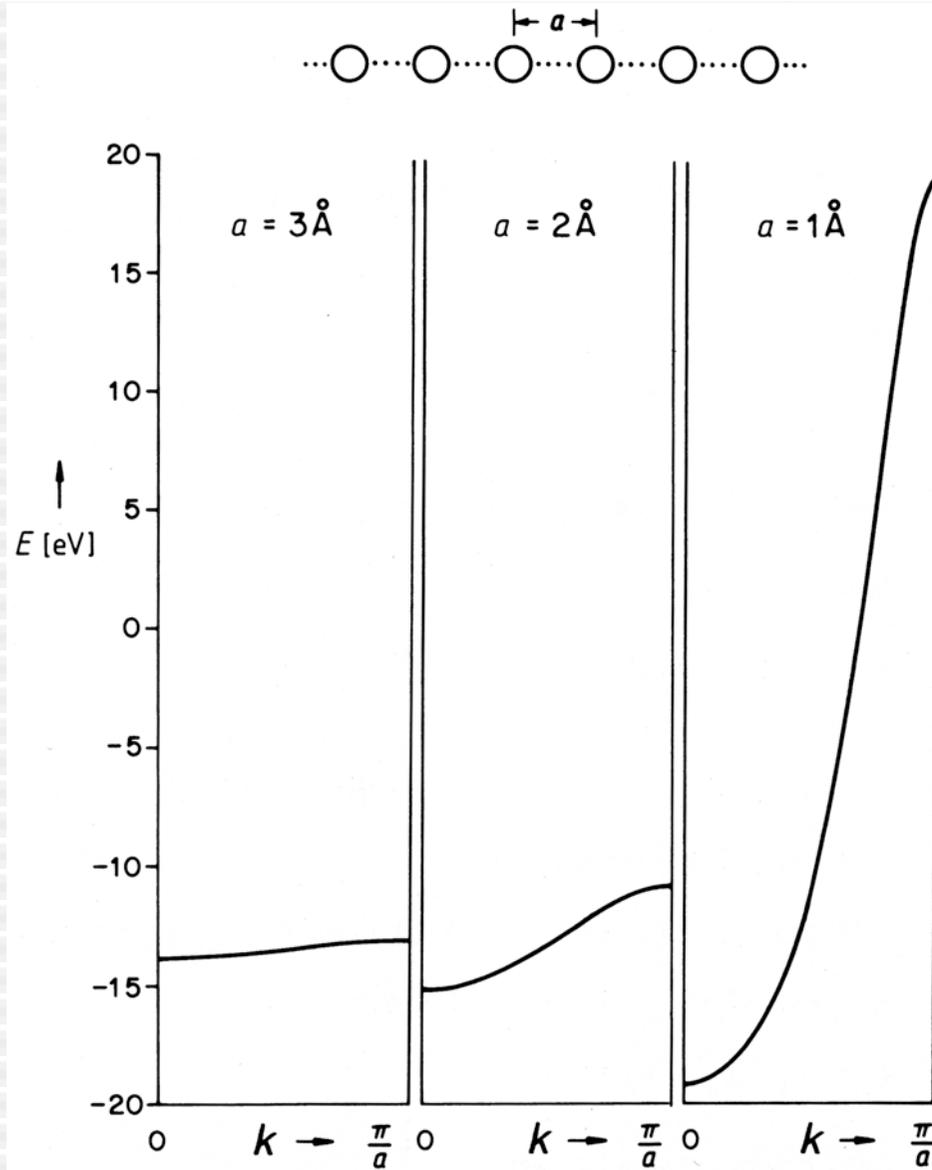
≡



≡

↑  
 $E$



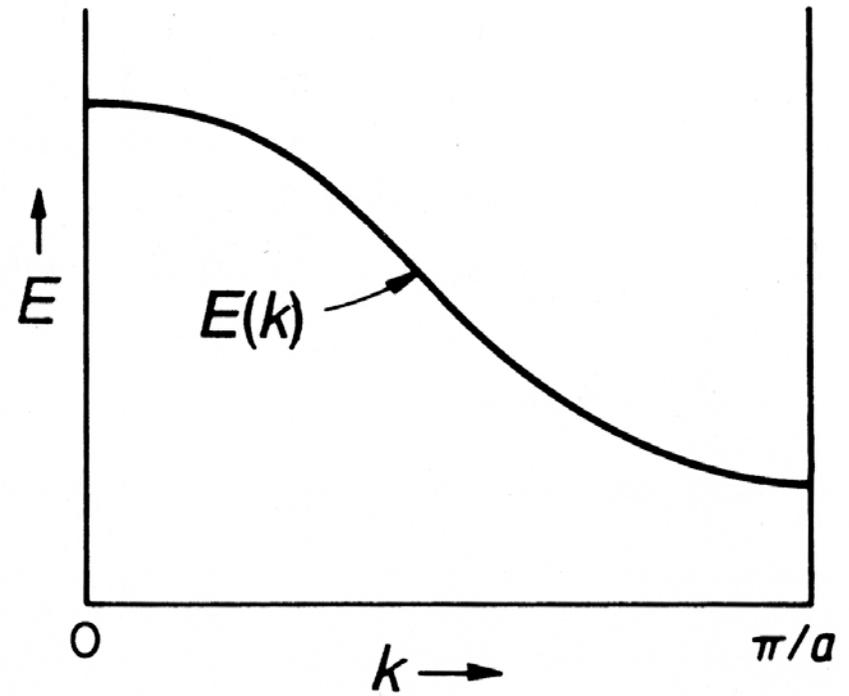


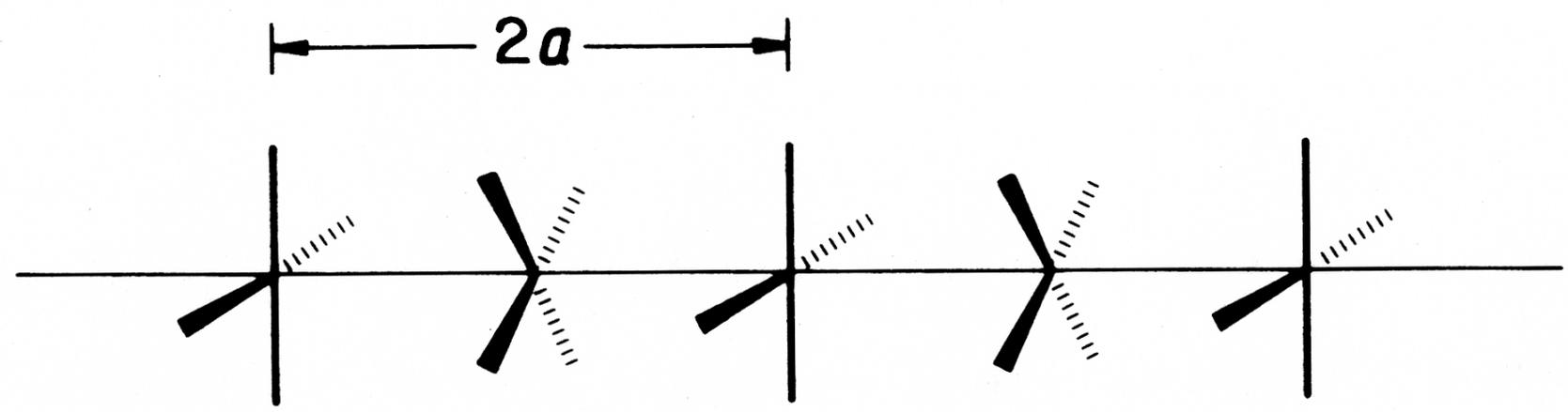
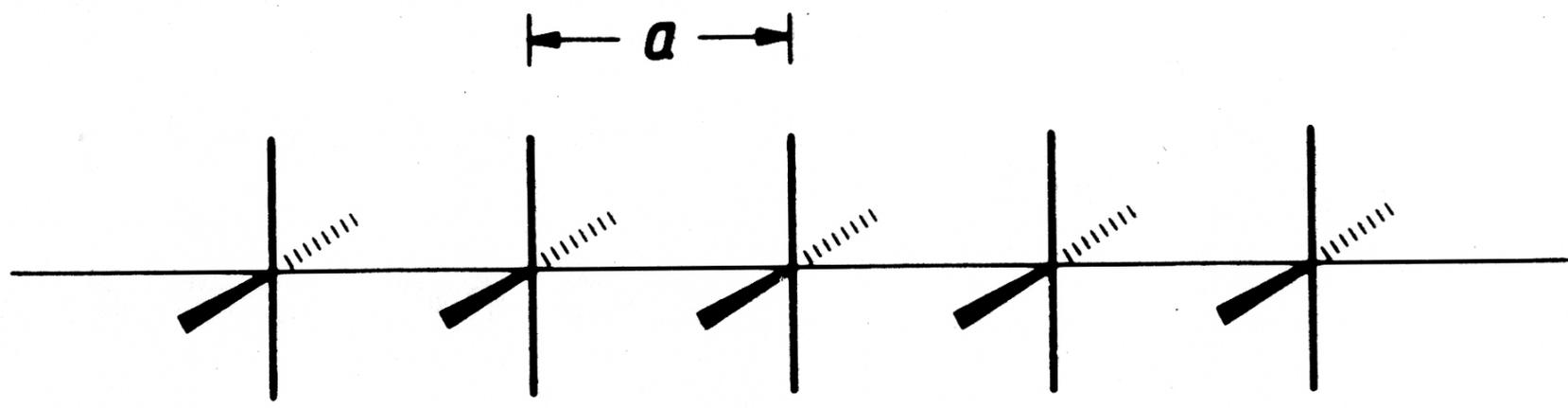
原子間距離  $a=3, 2, 1\text{\AA}$  としたときの水素原子鎖のバンド構造。孤立水素原子のエネルギーは  $-13.6\text{ eV}$  である。

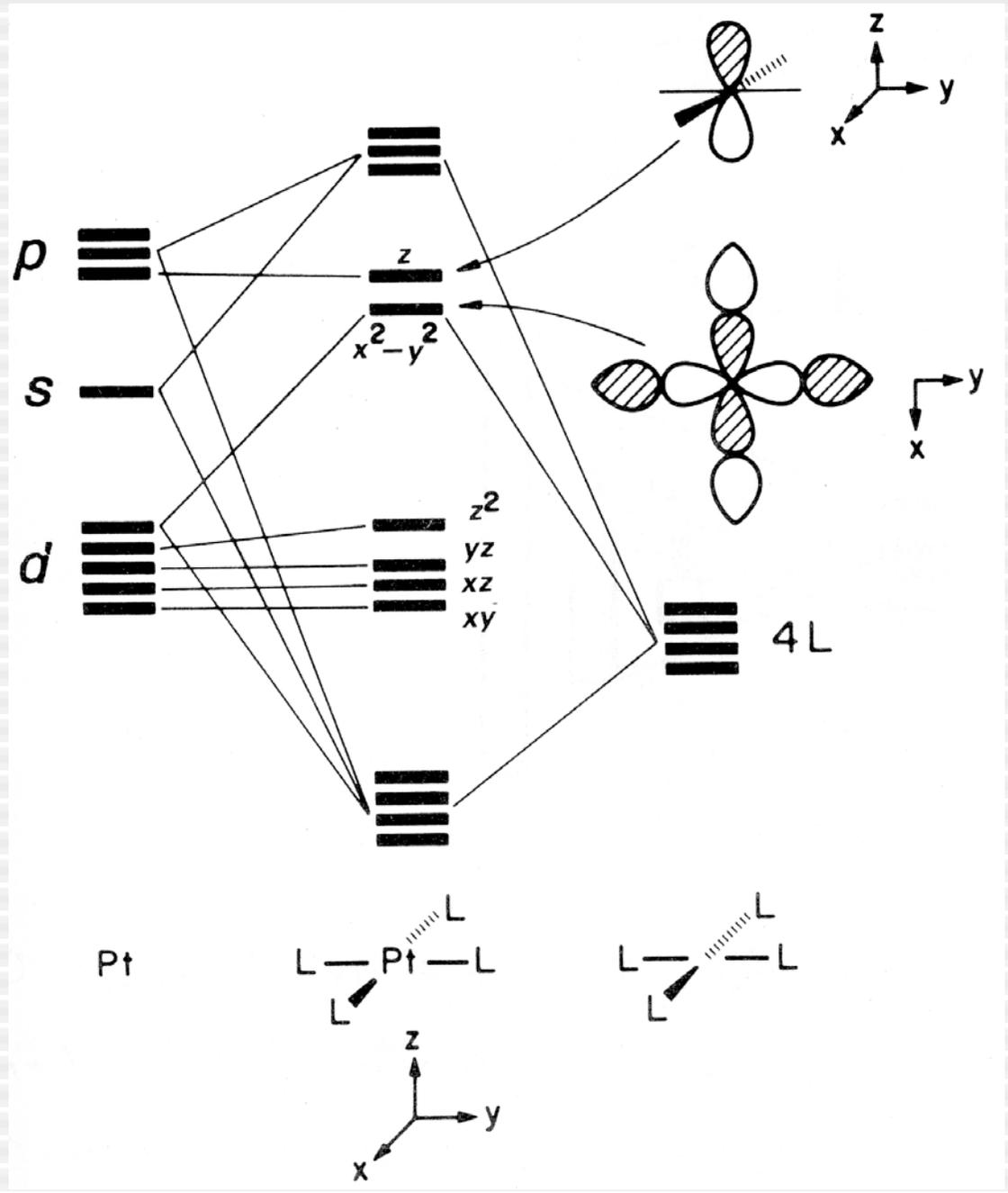
$$\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



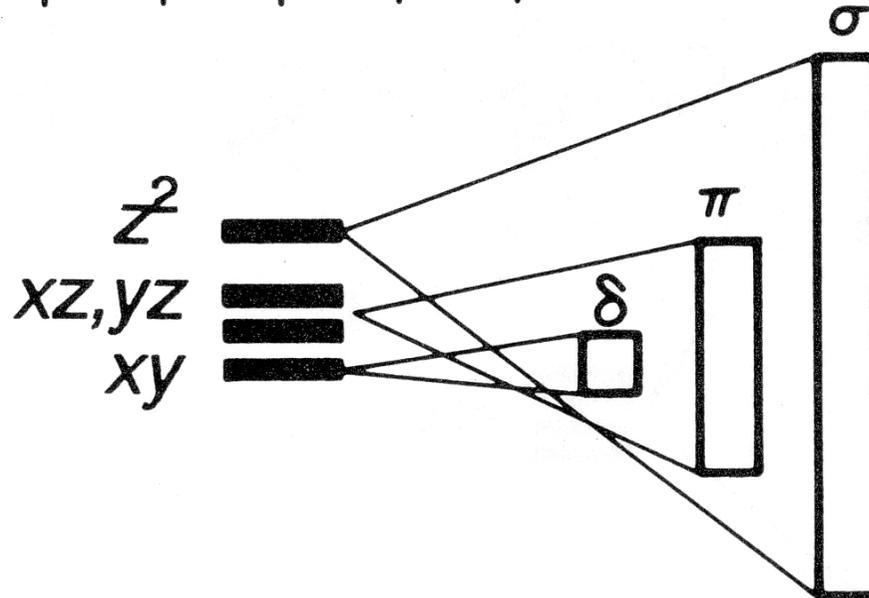
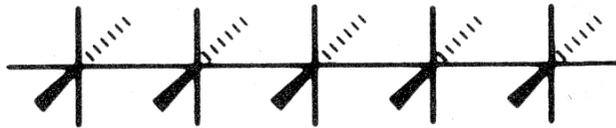
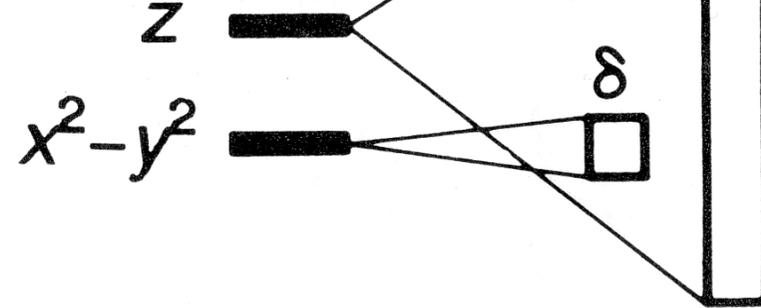
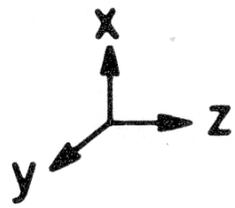
$$\psi_{\frac{\pi}{a}} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$

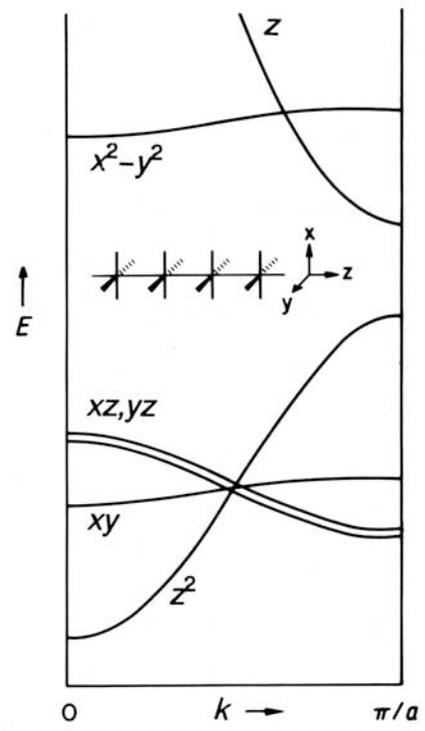
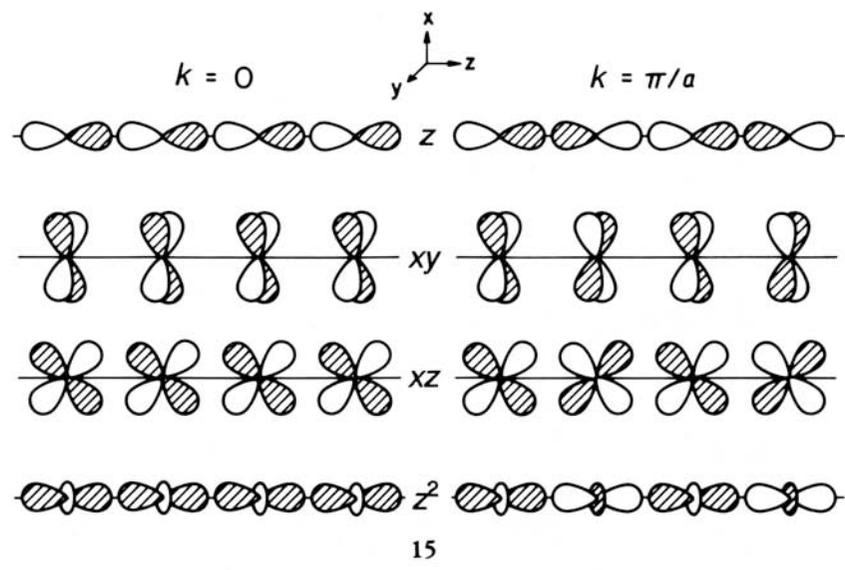


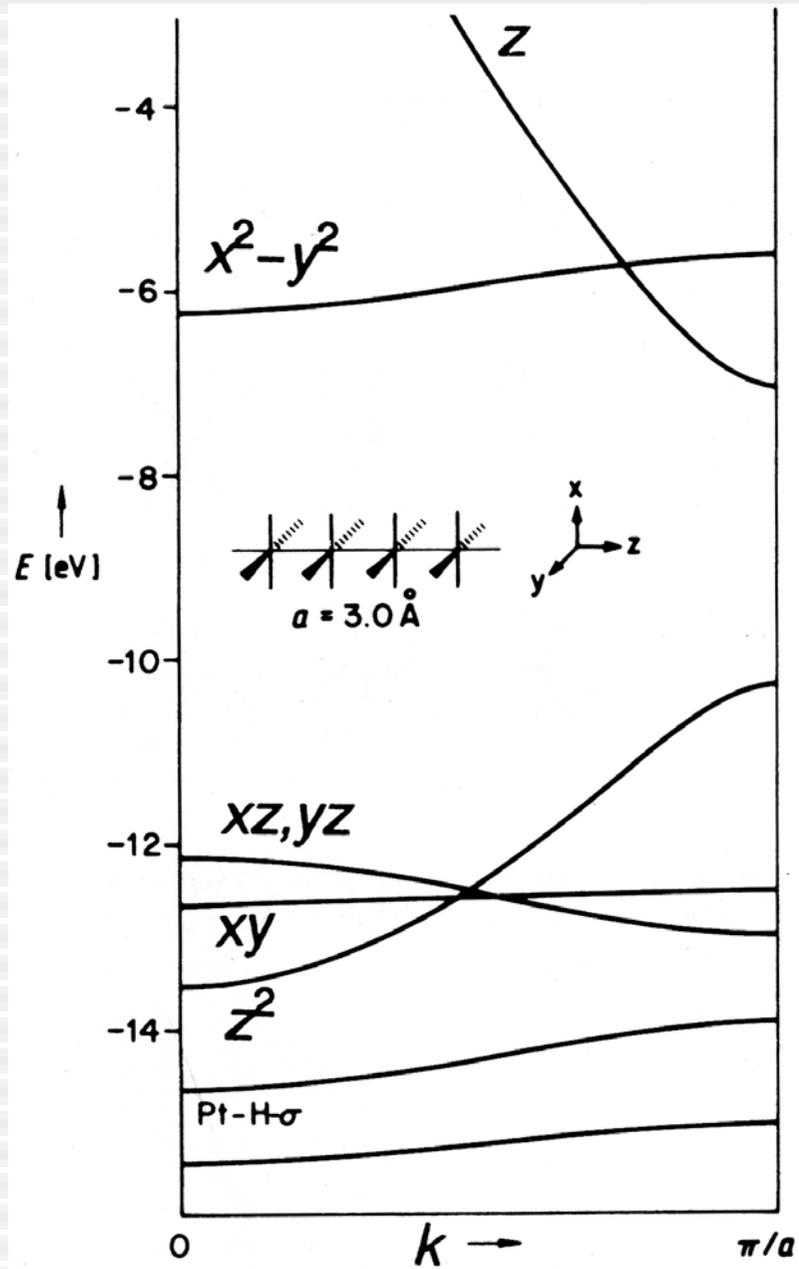


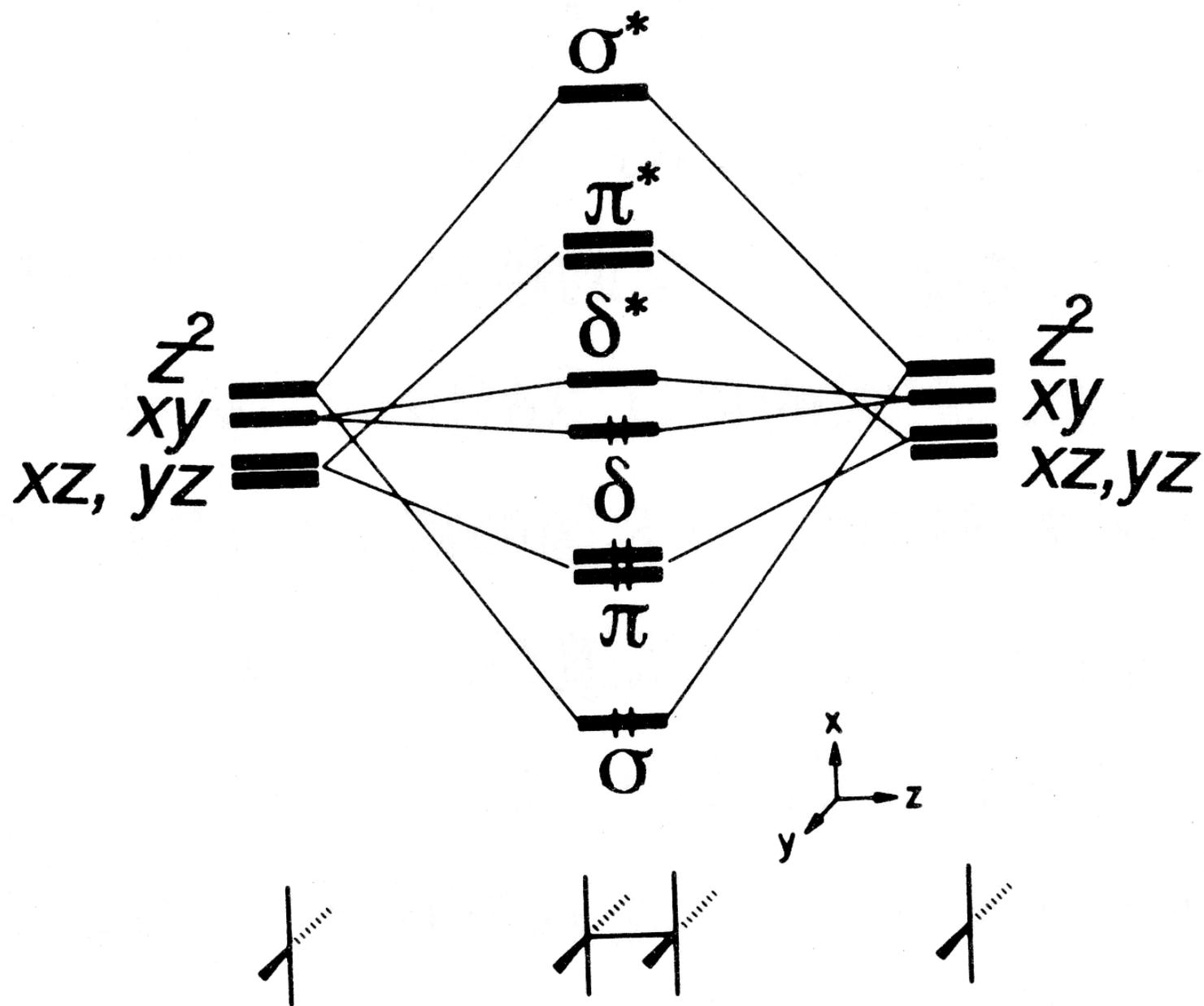


$E$  ↑



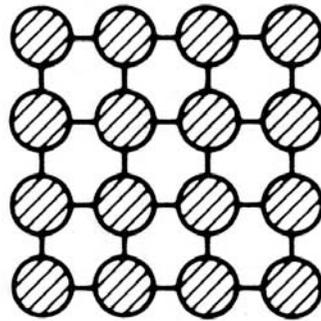




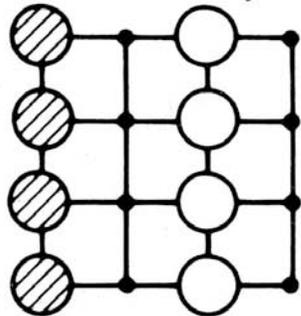


$\Gamma$

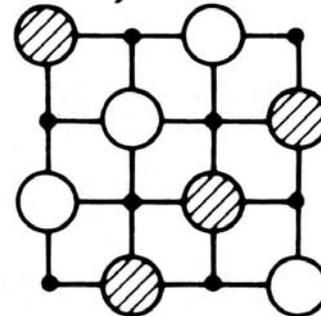
$$k_x = 0, k_y = 0$$



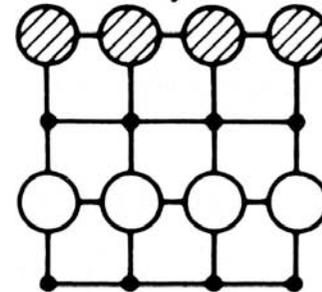
$$k_x = \pi/(2a), k_y = 0$$



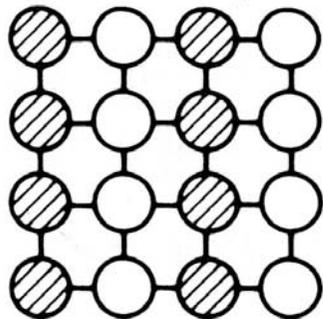
$$k_x, k_y = \pi/(2a)$$



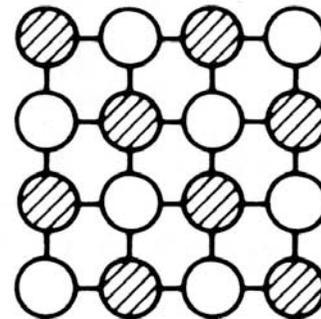
$$k_x = 0, k_y = \pi/(2a)$$



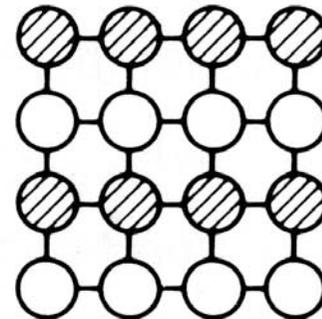
$$k_x = \pi/a, k_y = 0$$



$$k_x, k_y = \pi/a$$



$$k_x = 0, k_y = \pi/a$$



X

M

X

