分子性固体中の伝導性π電子
Conducting π electrons in molecular solids

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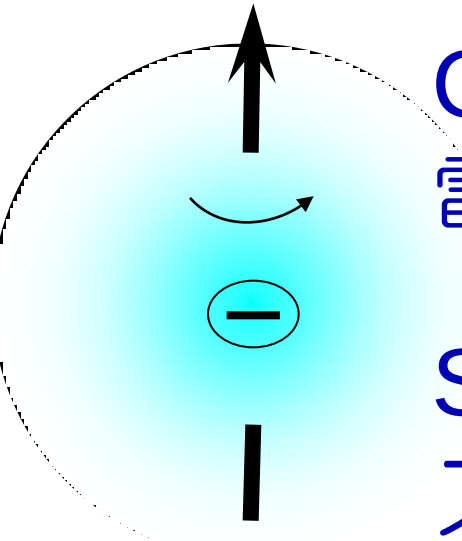
Fundamental Questions in Solid State Science

What are metals ?

What are magnets ?

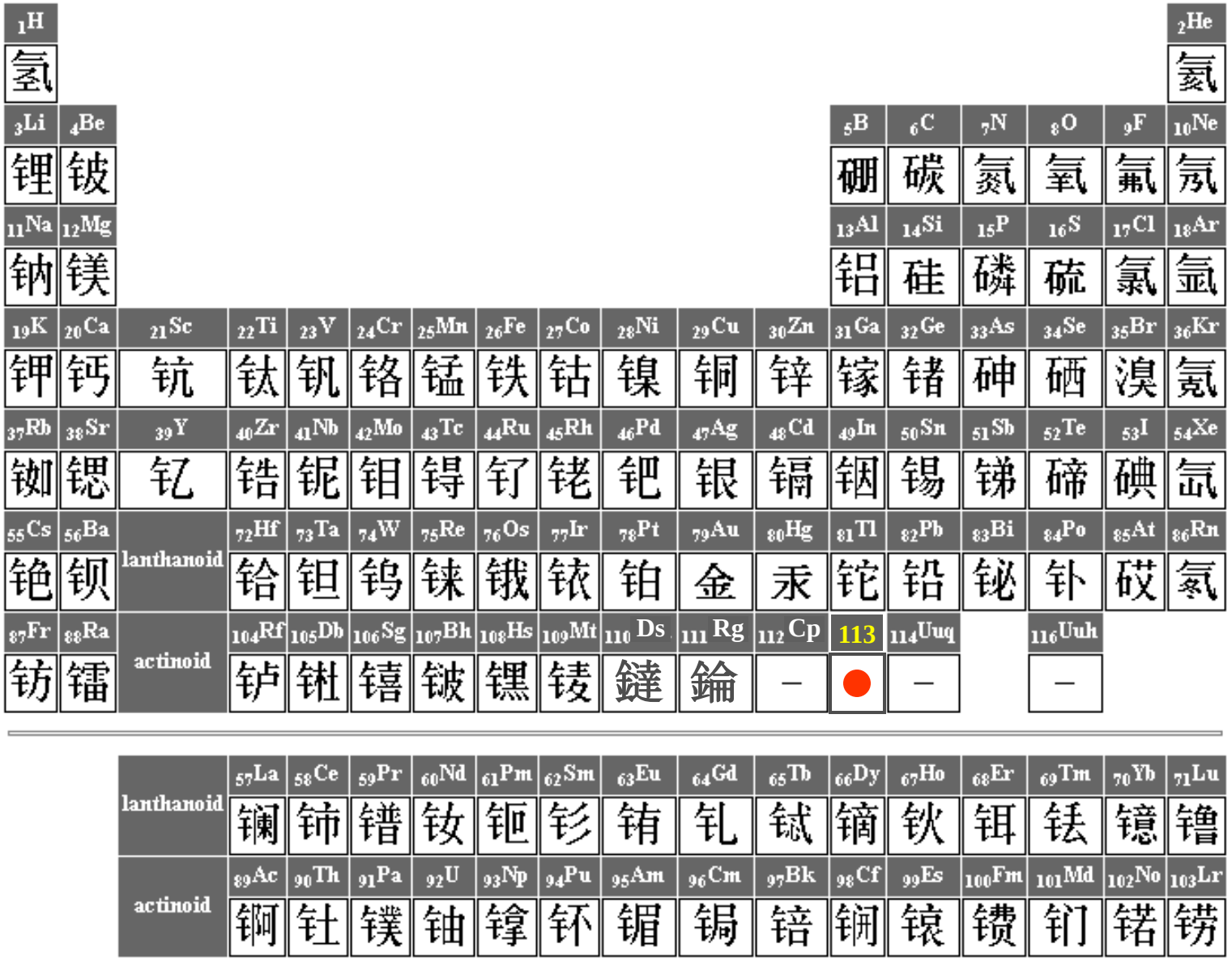


Charge
電荷

Spin
スピン

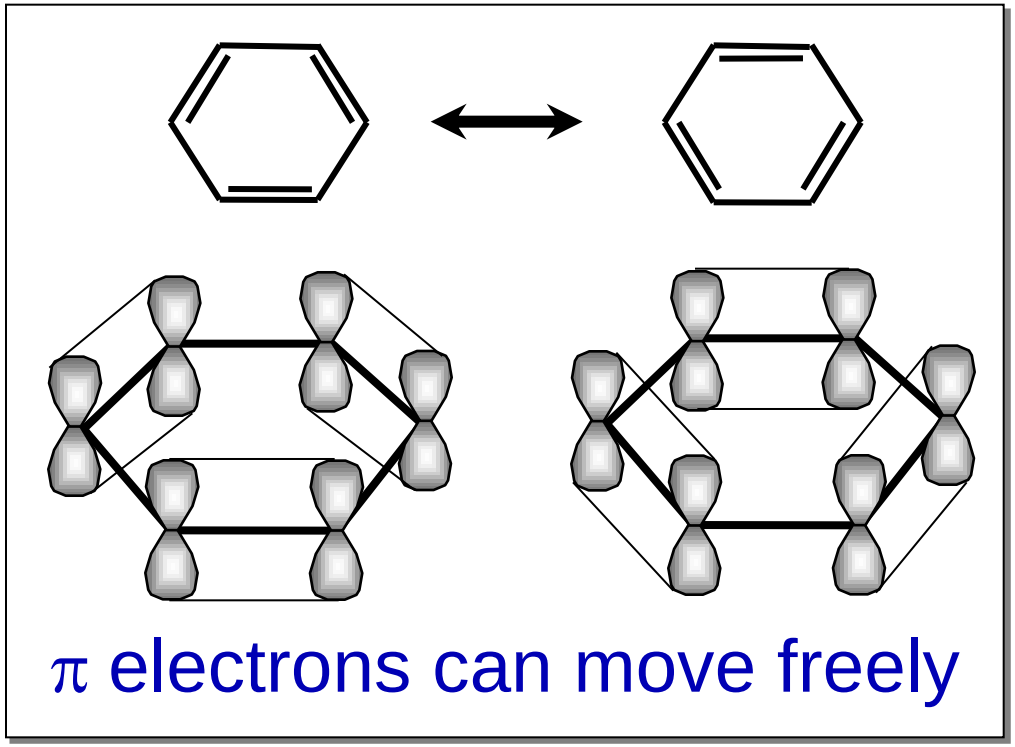
The *electron* is the lead of solid state science.

Chinese Periodic Table

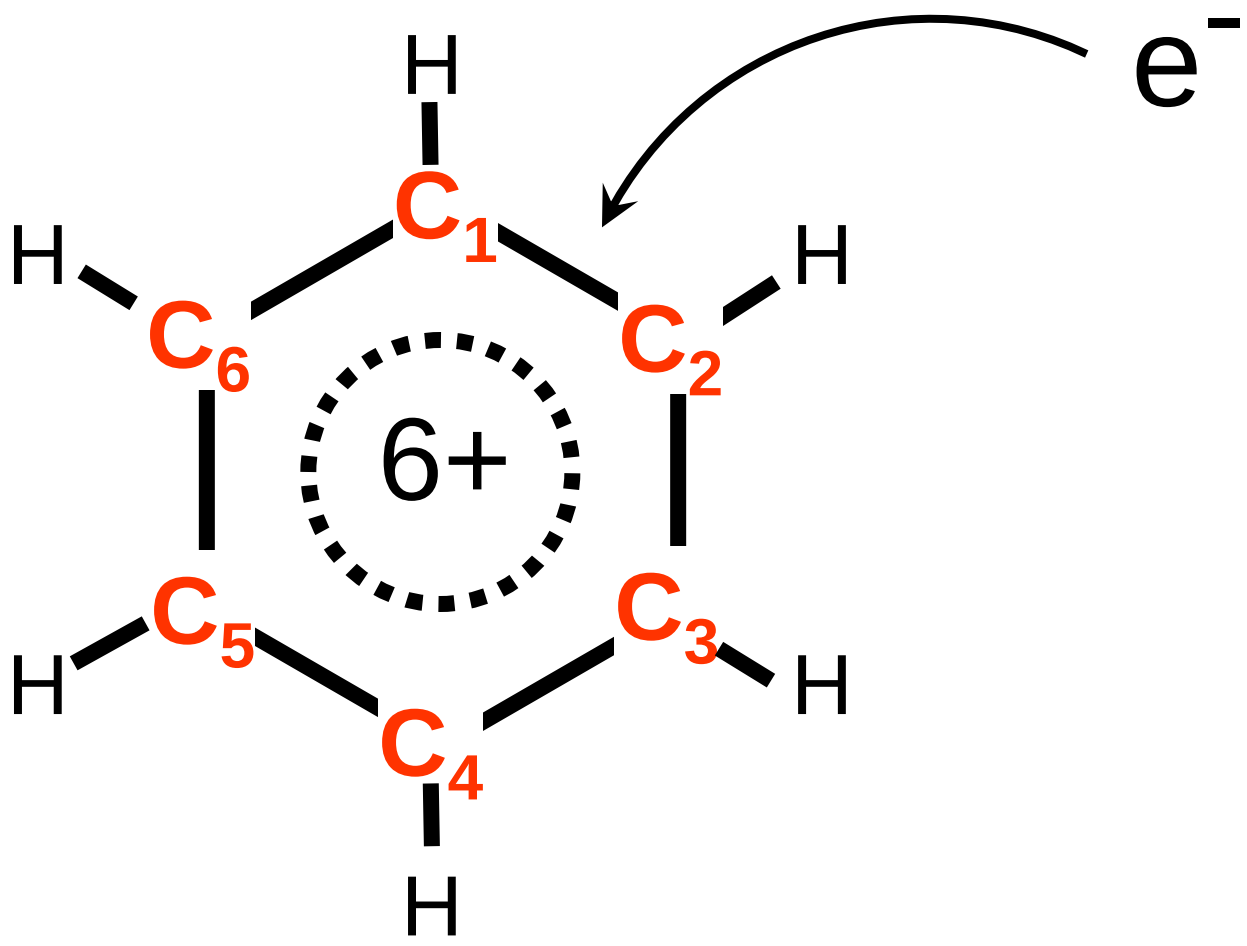


Metals from Non-metal Elements

Metals have conducting electrons which can move in a crystal freely and carry electricity and heat.



A π electron in benzene



Fundamental Principles (I)

The superposition of probability amplitudes （確率振幅の重ね合わせ）

$$\psi(t) = \sum_i C_i(t)\phi_i$$

ϕ_i: Base state

$C_i(t)$: Probability amplitude

Any state can be represented as a linear combination of a set of base states with suitable coefficients (probability amplitudes).

系の任意の状態は「ベクトル」のように「基本状態」の線形結合で表される。

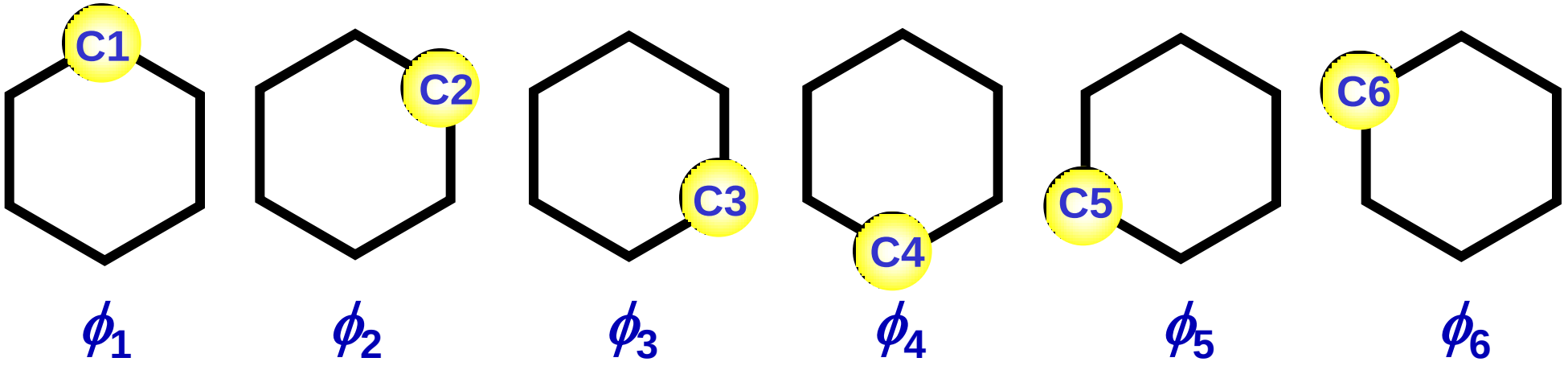
The probability P_i that the system is in the base state ϕ_i is the square of the absolute value of the probability amplitude C_i.

系が基本状態 ϕ_i にある確率P_iは、確率振幅C_iの絶対値の２乗。 $P_i = |C_i(t)|^2$

The probability amplitude is a complex number.

確率振幅は複素数。

Base states for a π electron in benzene



$$\psi(t) = \sum_{i}^{6} C_i(t)\phi_i$$

Fundamental Principles (II)

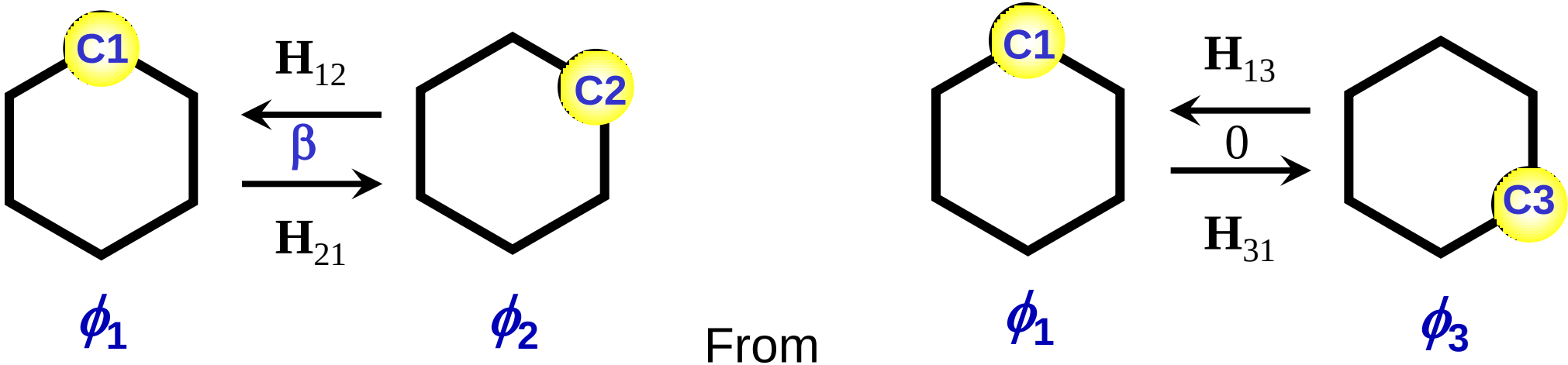
How the amplitudes vary with time

$$i\hbar \frac{\mathrm{d}C_i(t)}{\mathrm{d}t} = \sum_j \mathbf{H}_{ij} C_j(t)$$

H_{ij}: Hamiltonian matrix
（ハミルトニアン行列）

$-(i/\hbar)\mathbf{H}_{ij}$ is the amplitude that the base state j will be converted into the base state i during the time *dt.*
（基本状態 j が、時間 *dt* の間に、基本状態 i へ移る確率振幅）

H_{ij} in benzene ?

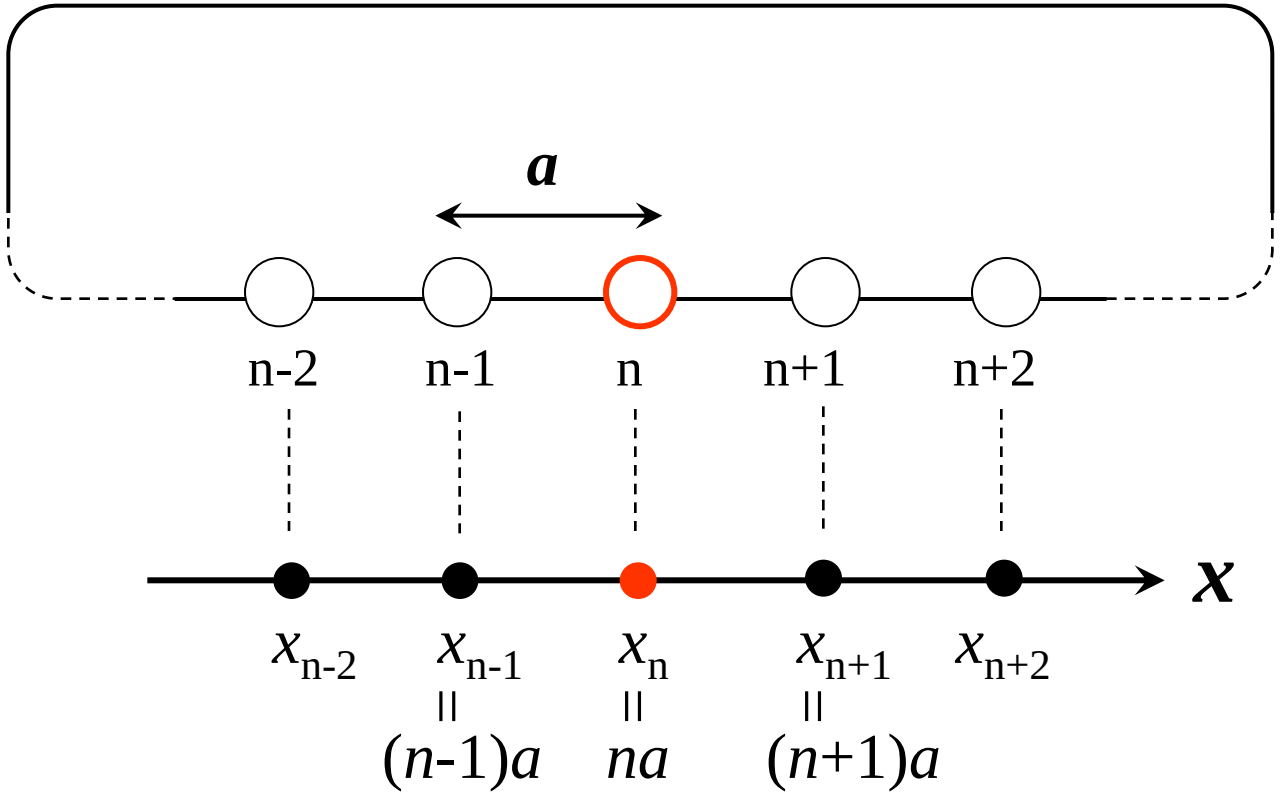


From

To

H_{ij}	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1	α	β	0	0	0	β
ϕ_2	β	α	β	0	0	0
ϕ_3	0	β	α	β	0	0
ϕ_4	0	0	β	α	β	0
ϕ_5	0	0	0	β	α	β
ϕ_6	β	0	0	0	β	α

N-membered Ring



$$i\hbar \frac{\mathrm{d}C_{\mathrm{n}}(t)}{\mathrm{d}t} = \alpha C_{\mathrm{n}}(t) + \beta C_{\mathrm{n+1}}(t) + \beta C_{\mathrm{n\text{-}1}}(t)$$

Fundamental Principles (III)

Stationary states （定常状態）

States in which all the amplitudes have the same time dependence $e^{-\frac{i}{\hbar}Et}$

確率振幅$C_i(t)$がすべて同じ時間依存性 $e^{-\frac{i}{\hbar}Et}$ を持つ状態

Stationary states are states of definite energy E.
この時、系は確定したエネルギー値 E を持つ。

$$C_i(t) = Ae^{-\frac{i}{\hbar}Et}$$

The wave traveling in the *x*-direction with the wave length λ

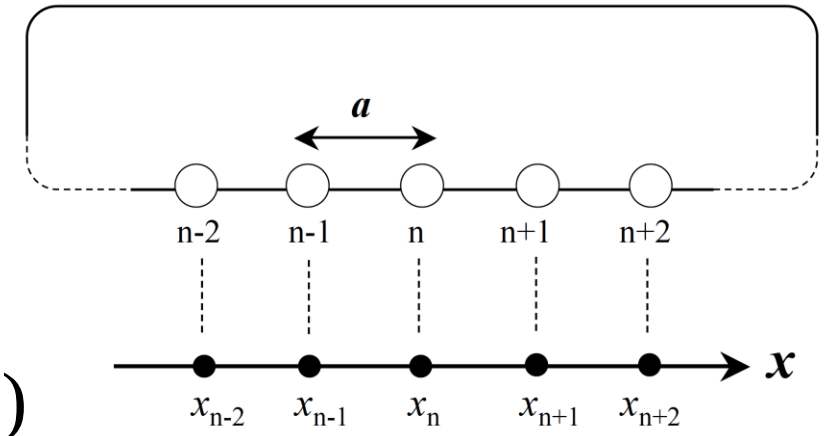
$$e^{ikx} \cdot e^{-i\omega t} = e^{ikx} \cdot e^{-\frac{i}{\hbar}Et}$$

$k = \frac{2\pi}{\lambda}$: wave number （波数）

$\hbar\omega = \frac{h\omega}{2\pi} = h\nu = E$ (←light quanta: Einstein)

N-membered Ring

$$i\hbar \frac{\mathrm{d}C_{\mathrm{n}}(t)}{\mathrm{d}t} = \alpha C_{\mathrm{n}}(t) + \beta C_{\mathrm{n+1}}(t) + \beta C_{\mathrm{n-1}}(t)$$



In the stationary state, $C_{\mathrm{n}}(t) = A(x_{\mathrm{n}})e^{-\frac{i}{\hbar}Et}$

$$EA(x_{\mathrm{n}}) = \alpha A(x_{\mathrm{n}}) + \beta A(x_{\mathrm{n+1}}) + \beta A(x_{\mathrm{n-1}})$$
$$= \alpha A(x_{\mathrm{n}}) + \beta A(x_{\mathrm{n}} + a) + \beta A(x_{\mathrm{n}} - a)$$

Let's take as a trial solution $A(x_{\mathrm{n}}) = A_{\mathrm{o}} e^{ikx_{\mathrm{n}}}$ (the space dependence of the amplitudes)

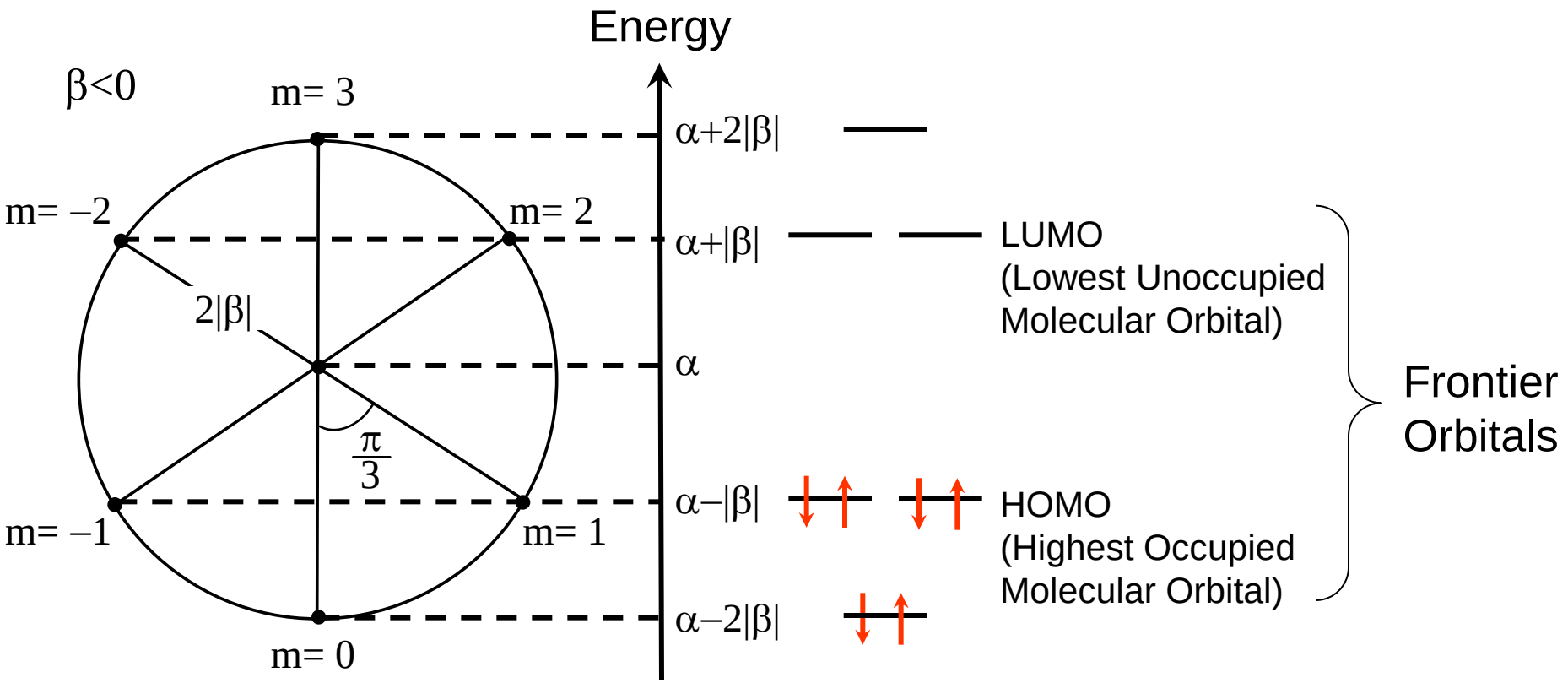
$$E(k) = \alpha + \beta e^{ika} + \beta e^{-ka} = \boxed{\alpha + 2\beta \cos ka}$$

$$A(x_{\mathrm{n+N}}) = A(x_{\mathrm{n}} + Na) = e^{ik(x_{\mathrm{n}}+Na)} = A(x_{\mathrm{n}}) = e^{ikx_{\mathrm{n}}}$$

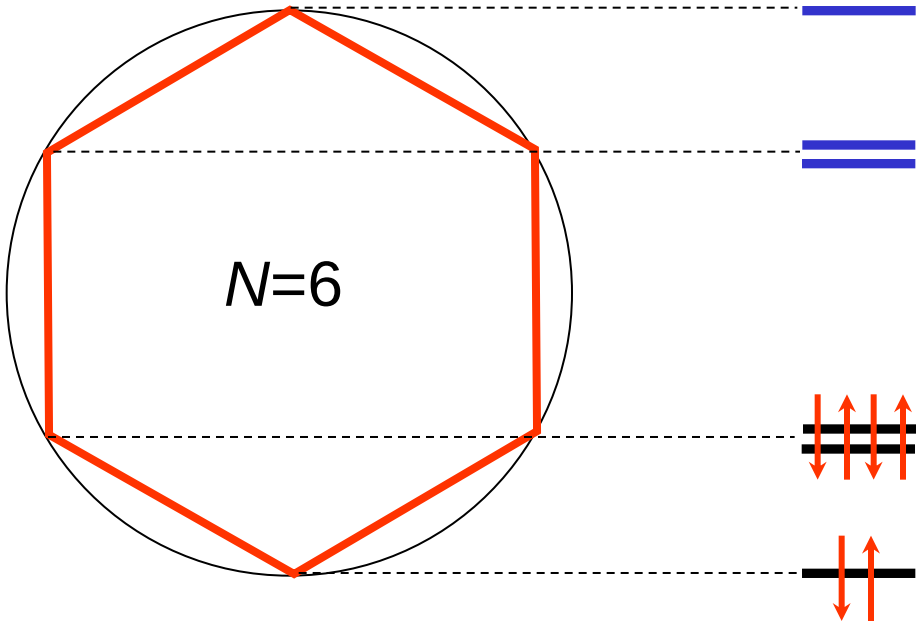
$$\therefore e^{ikNa} = 1 \quad i.e. \quad \boxed{k = \frac{2\pi}{a} \cdot \frac{1}{N} \cdot m} \quad \text{for integral } m$$

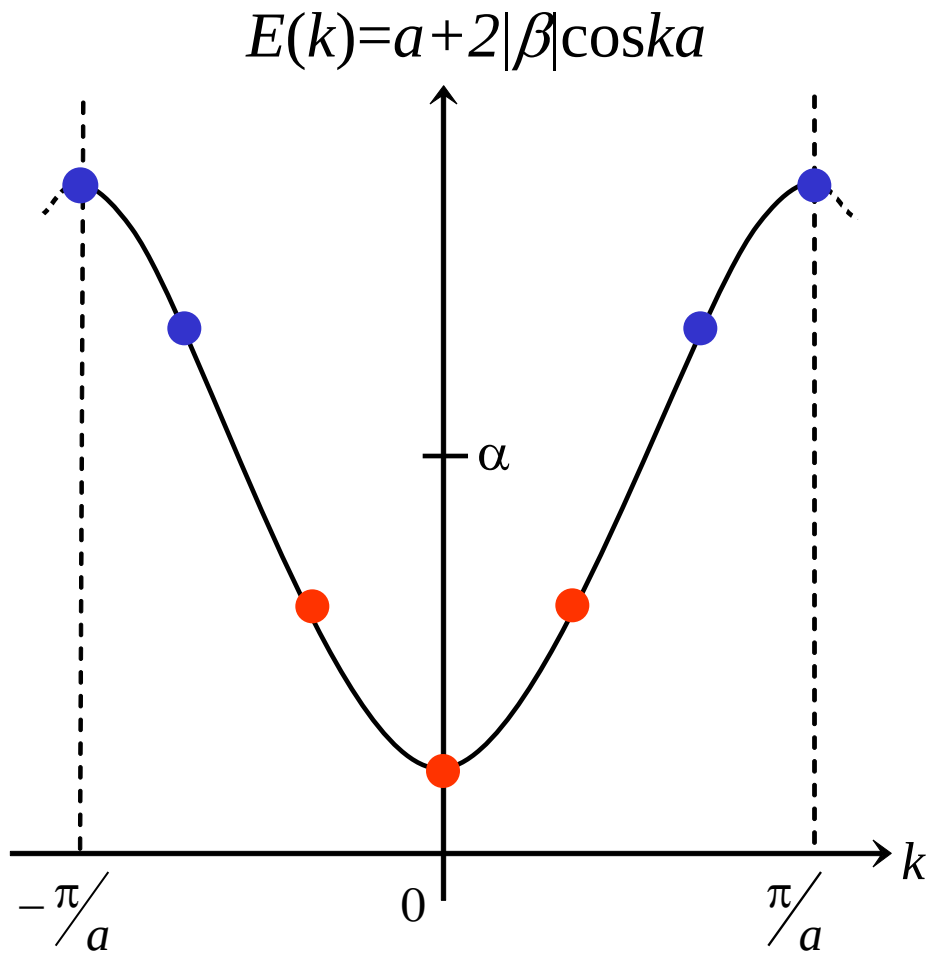
Energy levels in benzene

$$\left.\begin{aligned} E(k) &= \alpha + 2\beta\cos ka \\ k &= \frac{2\pi}{a}\cdot\frac{1}{N}\cdot m = \frac{2\pi}{a}\cdot\frac{1}{6}\cdot m \end{aligned}\right\} \quad E = \alpha + 2\beta\cos\left(\frac{\pi}{3}m\right)$$

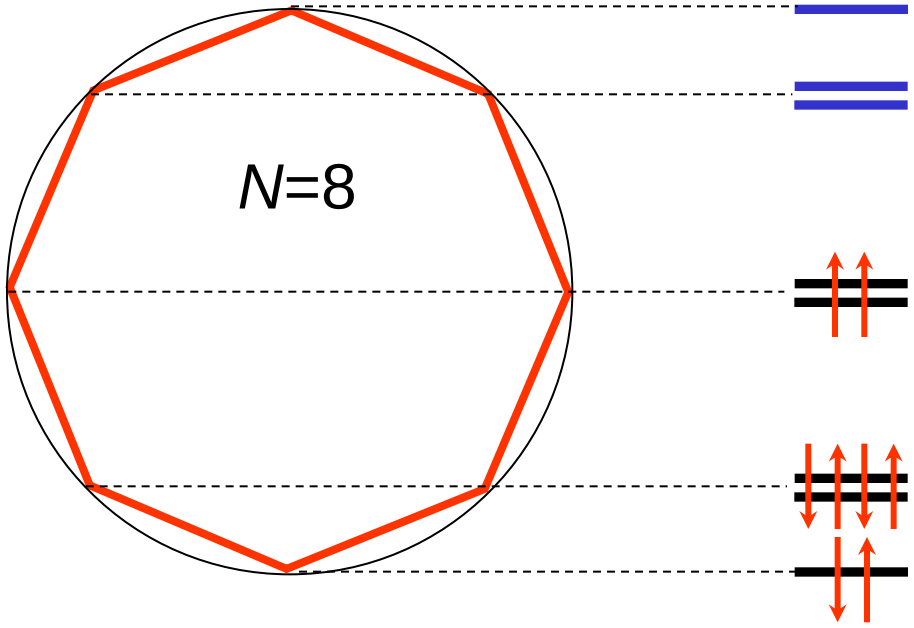


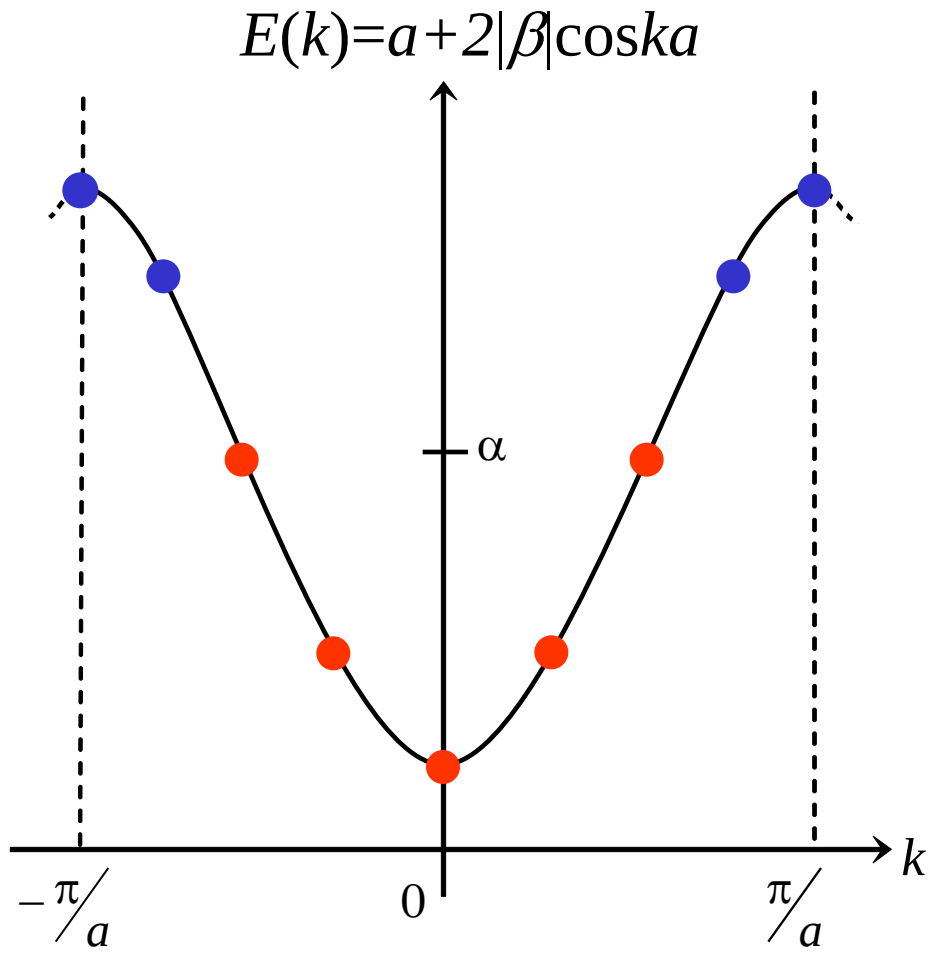
Energy levels (N = 6)



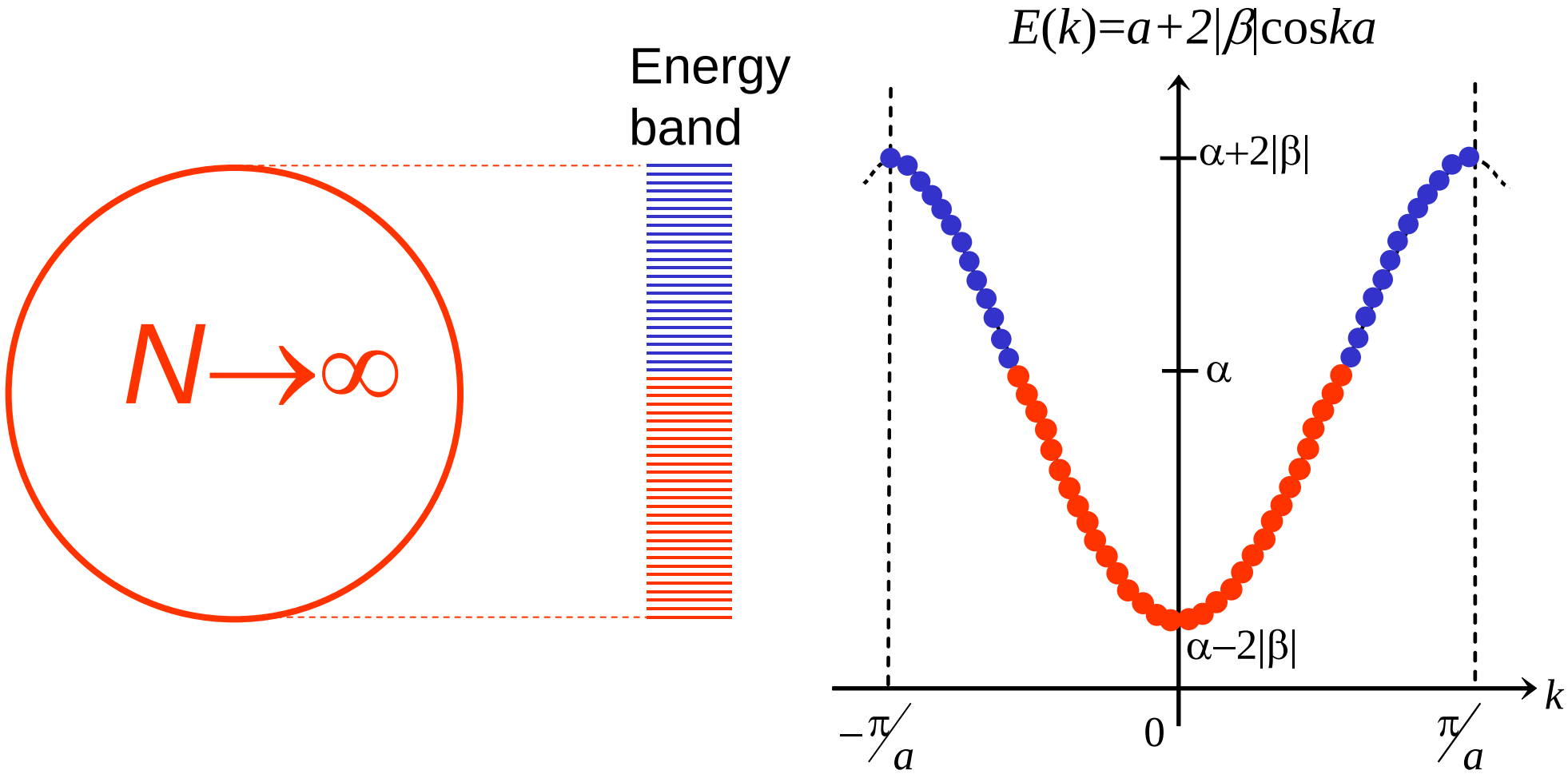


Energy levels (N = 8)



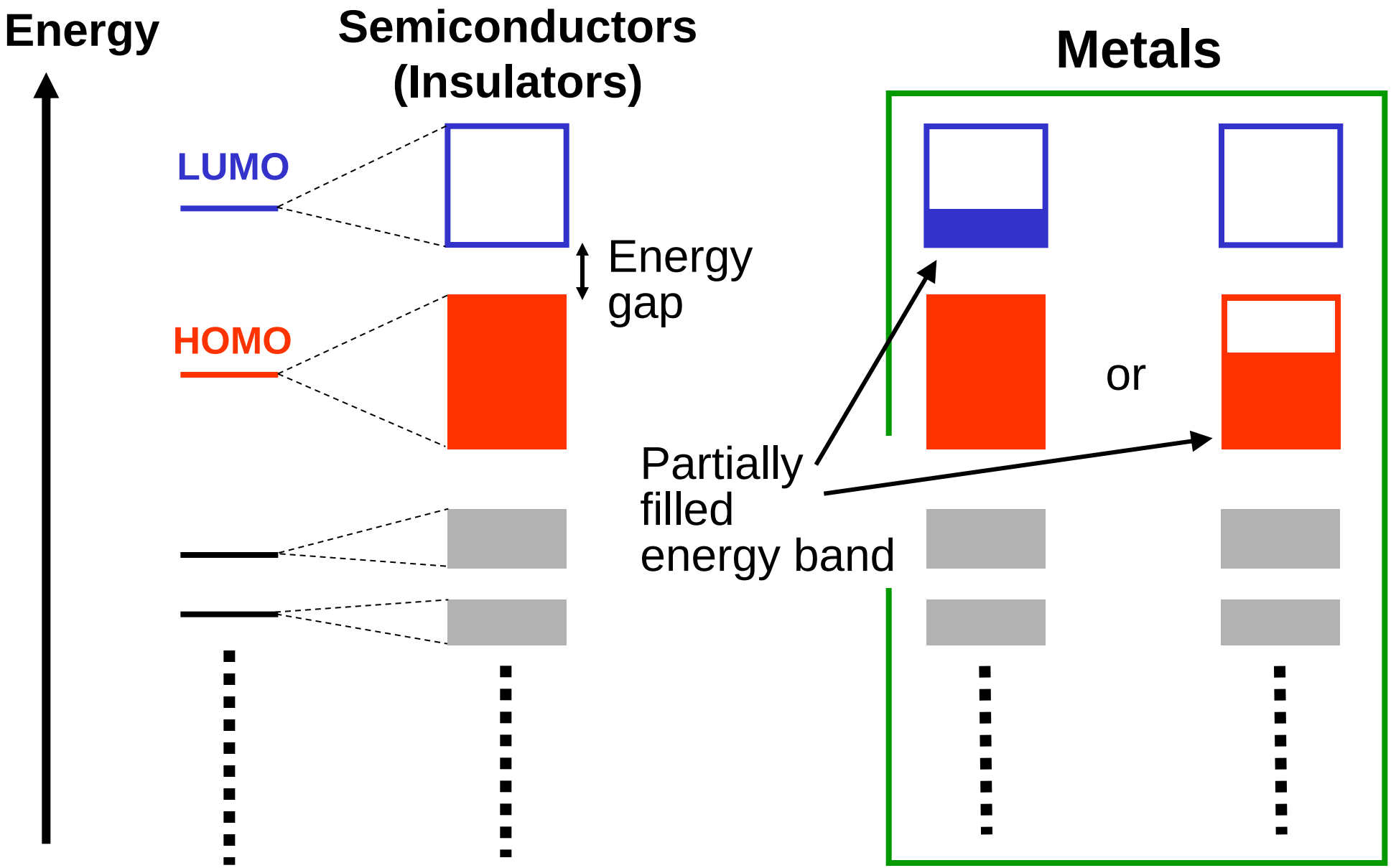


$N \to \infty$: Energy band



One-dimensional (uniform) lattice

What are metals ?



The Nobel Prize in Chemistry (2000)

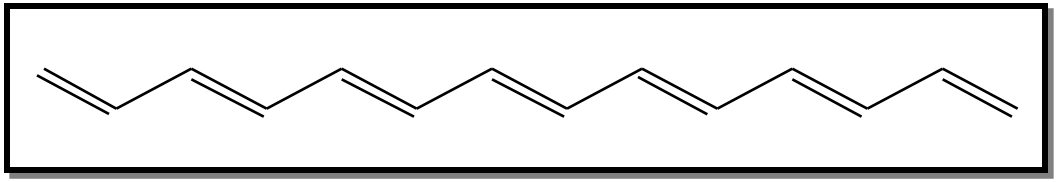
Conductive polymers

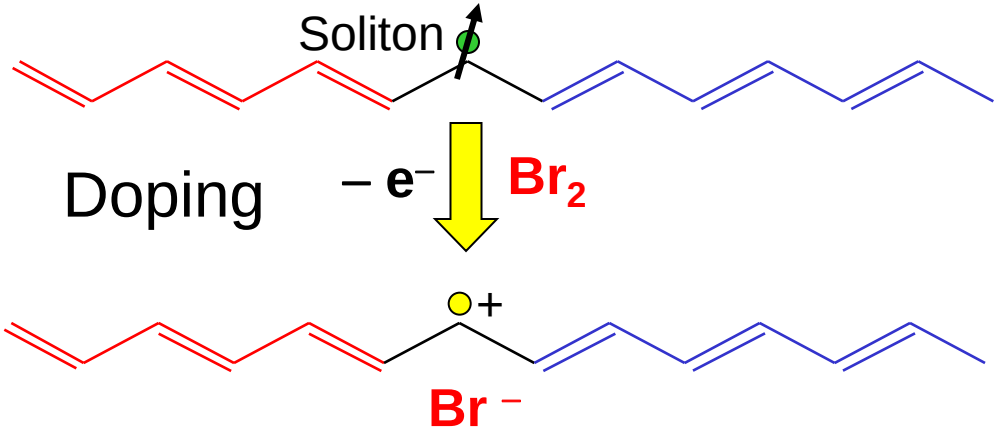
Polyacetylene film

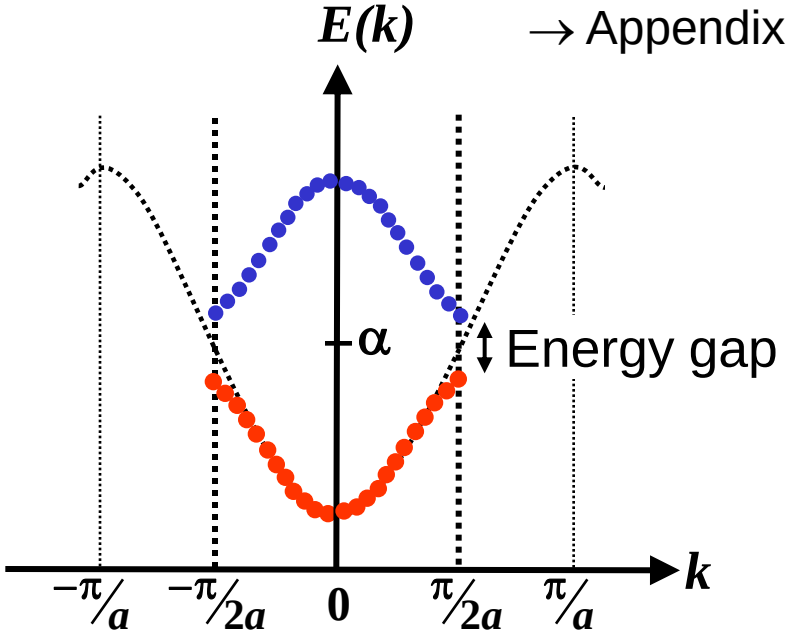
Hideki Shirakawa

Alan J. Heeger

Alan G. MacDiarmid

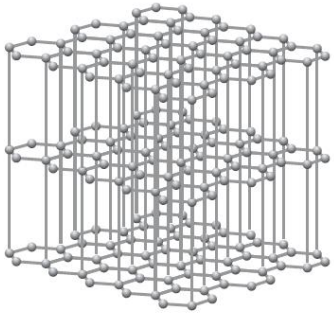






The Nobel Prize in Physics (2010)

Graphite



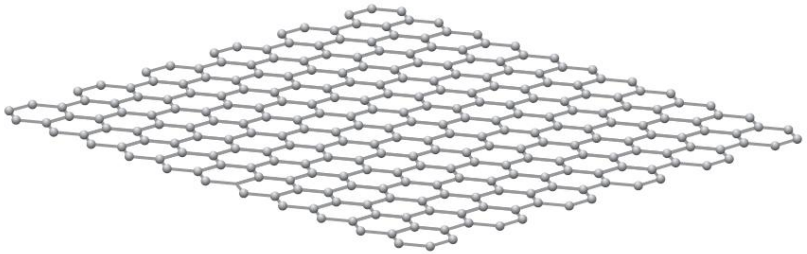
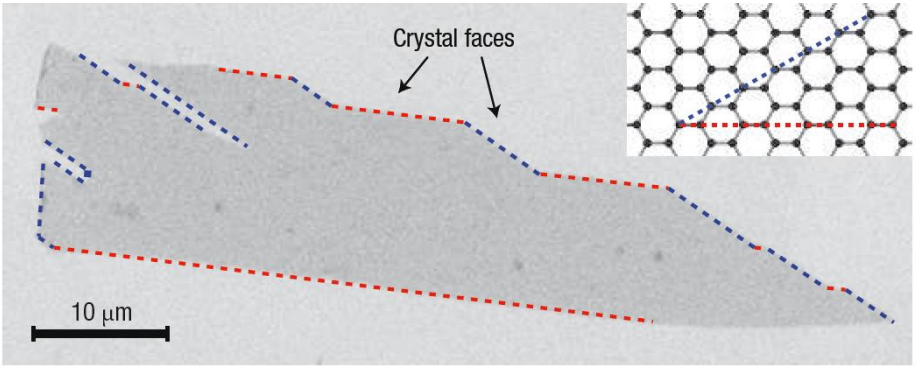


Photo: Sergeom, Wikimedia Commons

Andre Geim

Photo: University of Manchester, UK

Konstantin Novoselov



Graphene (Two-dimensional crystal)

Description of crystals
-Lattice and repeated unit-

A (Bravais) **lattice** is an infinite array of discrete points （離散的な点）

(a) with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.
どこの点から配列を眺めてみても、その配列と配向が全く同一

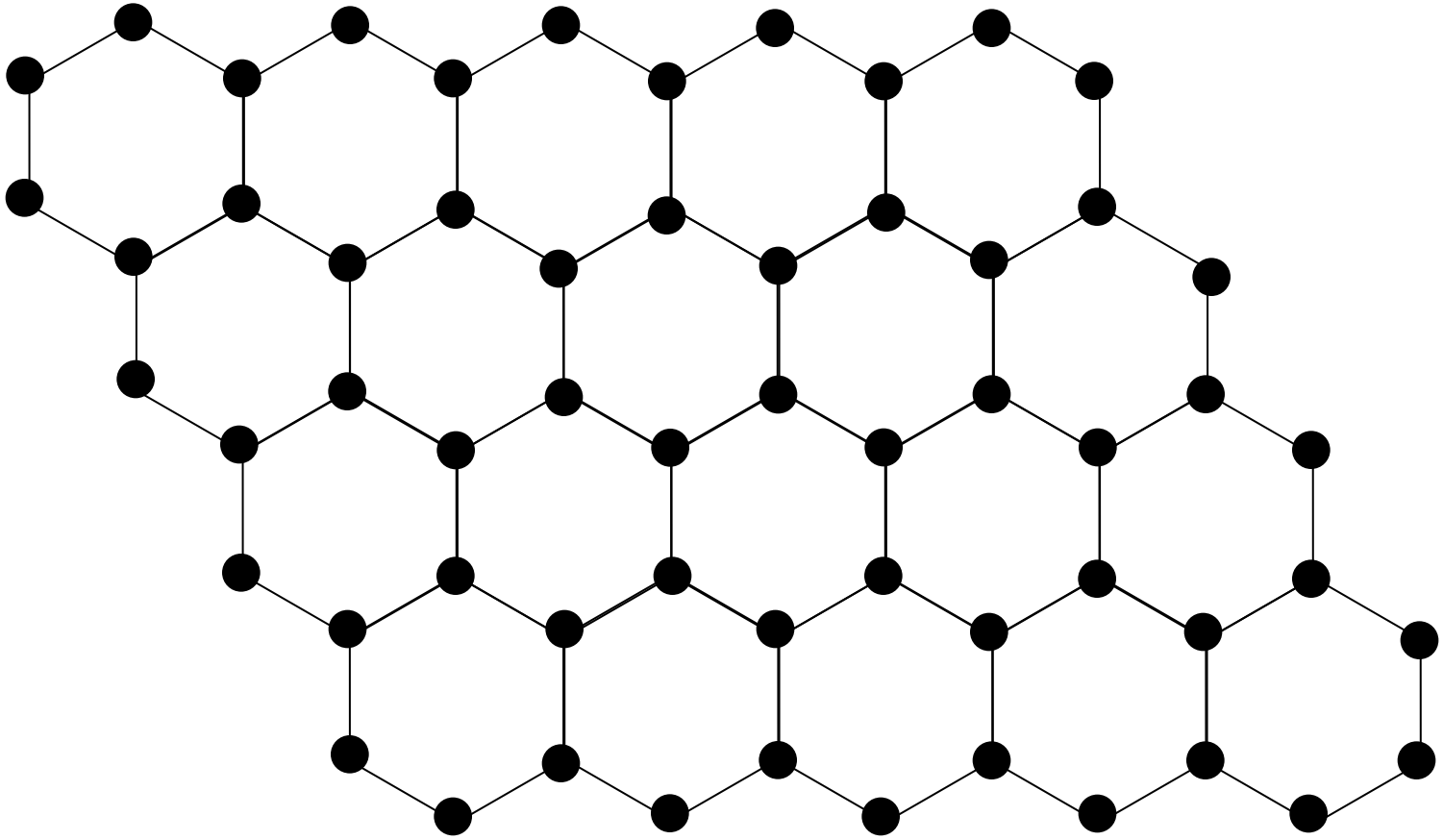
(b) with position vectors （位置ベクトル）**r** of the form

$$\mathbf{r} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$ for integral n_1, n_2, and n_3

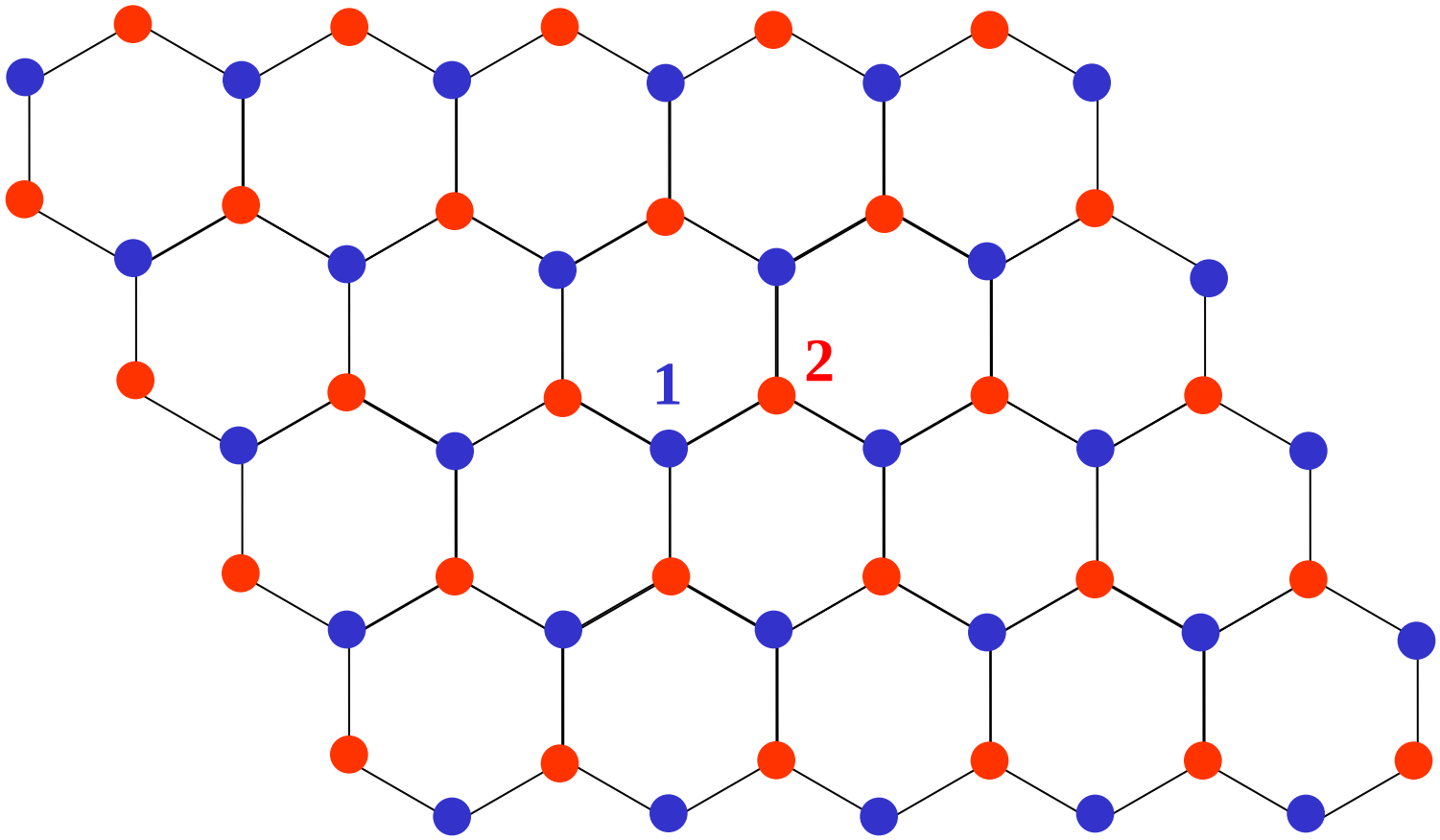
a, b, c: Primitive vectors

A Bravais lattice specifies the periodic array in which the repeated units are arranged.
ブラベー格子は繰り返し単位の周期配列を特徴付ける。

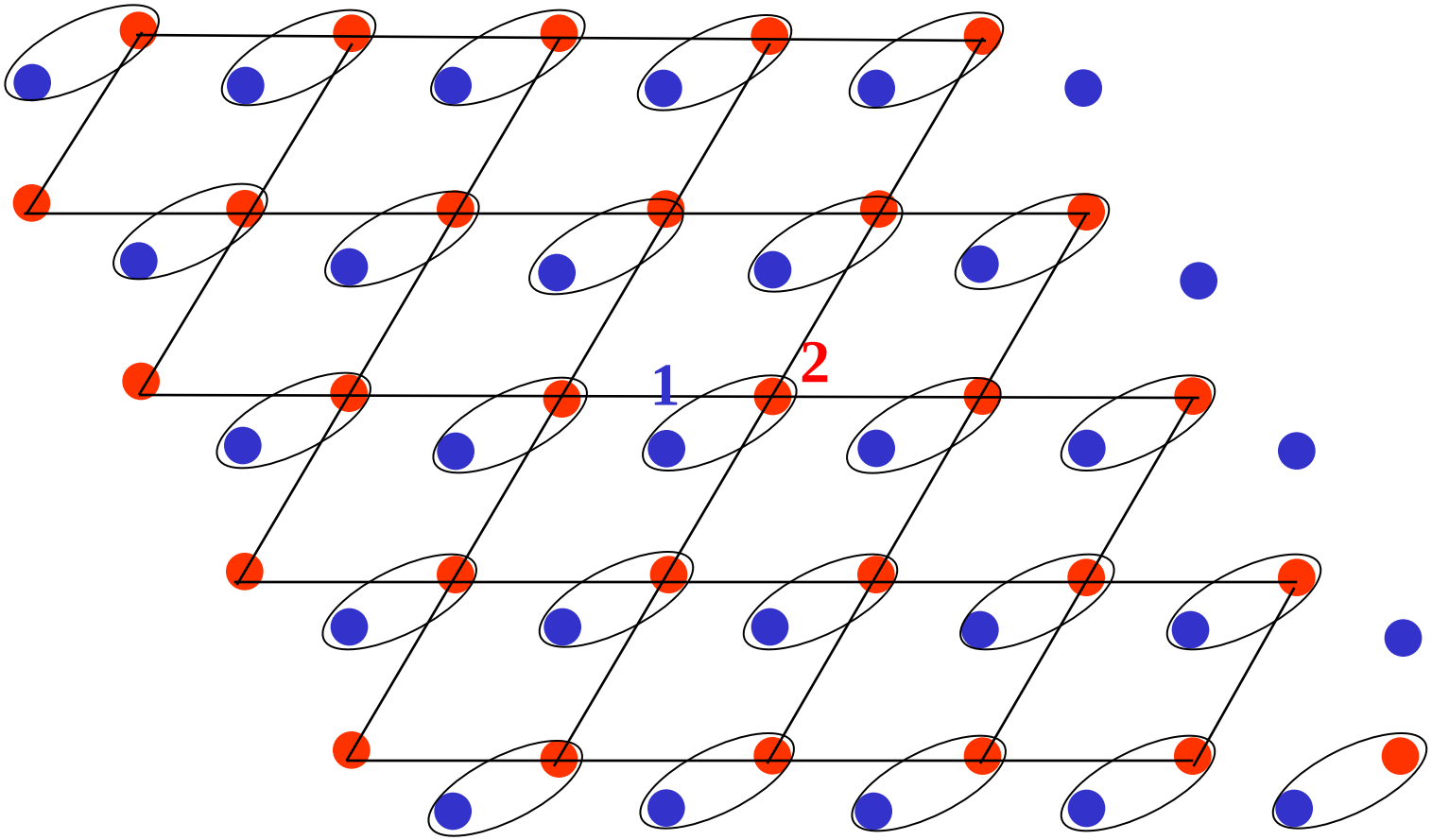
Is this a (Bravais) lattice ?



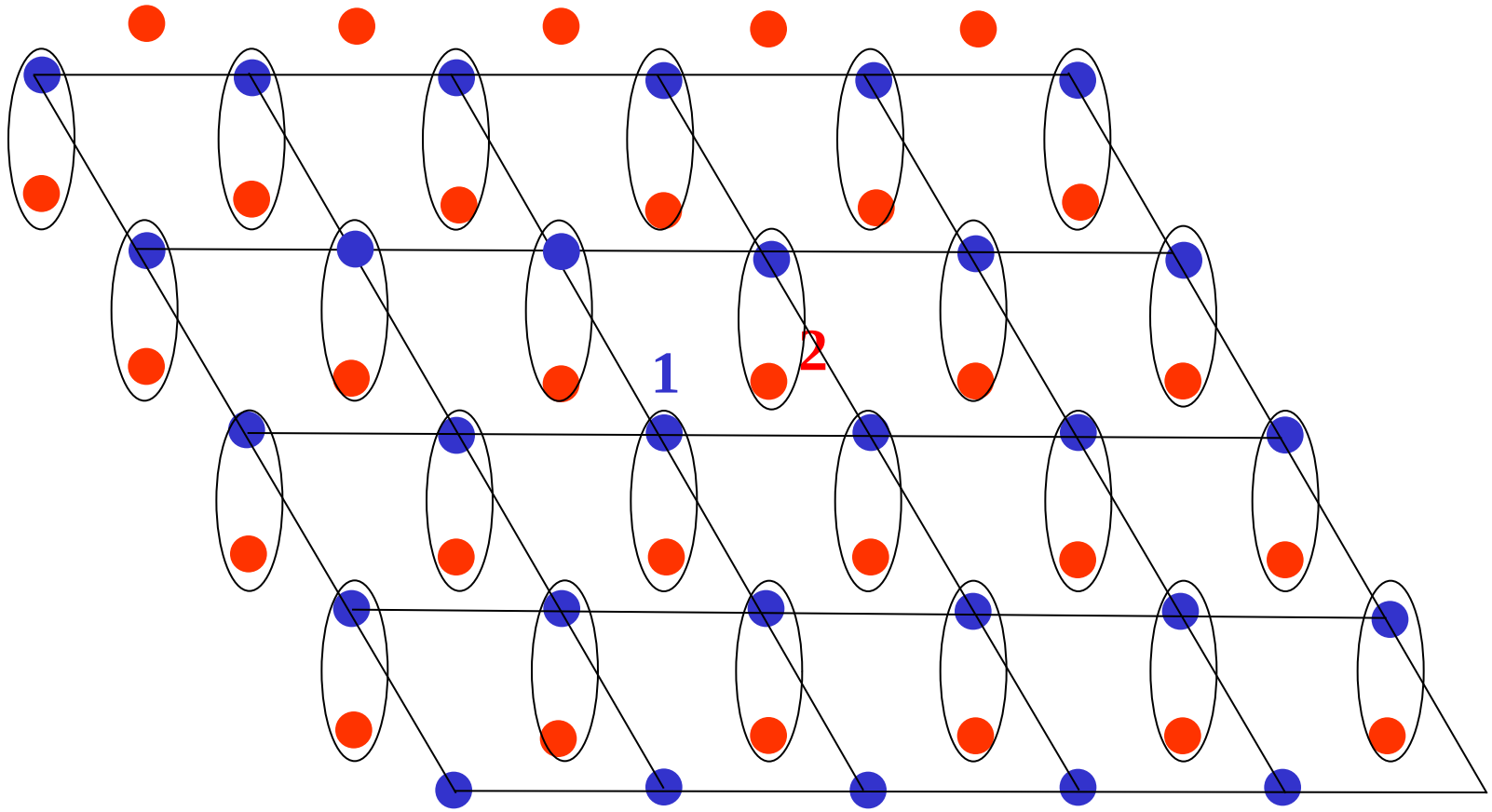
What is a repeated unit ?



How to describe Graphene crystal



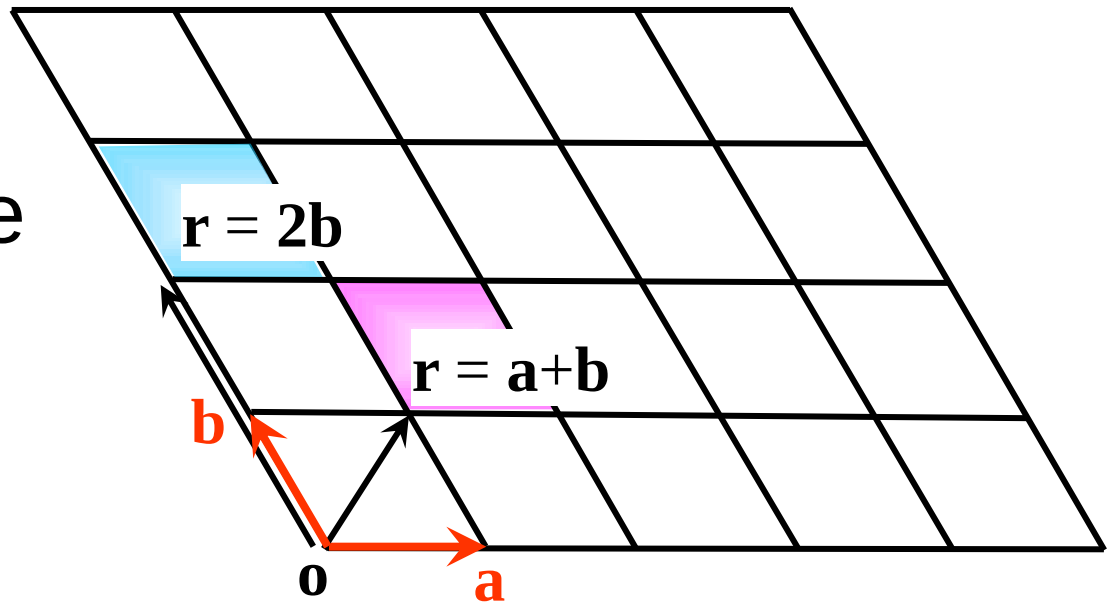
Another description



Graphene crystal

Graphene crystal =

Lattice



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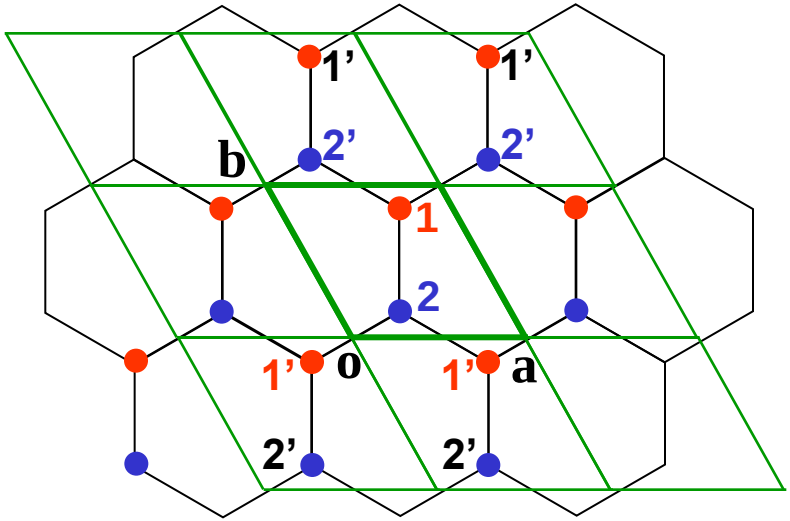
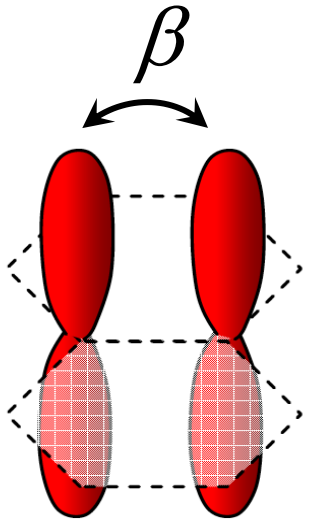
Repeated unit

How the amplitudes vary with time in graphene ?





$$\begin{cases} i\hbar \dfrac{dC_{1,\mathbf{o}}}{dt} = \beta C_{2,\mathbf{o}} + \beta C_{2,\mathbf{b}} + \beta C_{2,(\mathbf{a}+\mathbf{b})} \\ i\hbar \dfrac{dC_{2,\mathbf{o}}}{dt} = \beta C_{1,\mathbf{o}} + \beta C_{1,-\mathbf{b}} + \beta C_{1,-(\mathbf{a}+\mathbf{b})} \end{cases}$$

(The origin of the energy level is chosen so that α is zero.)

Energy band for graphene

In the stationary state, $C_{i,\mathbf{r}}(t) = A_i(\mathbf{r}_n)\cdot e^{-\frac{i}{\hbar}Et}$

$$\begin{cases} EA_1(\mathbf{o}) = \beta A_2(\mathbf{o}) + \beta A_2(\mathbf{b}) + \beta A_2(\mathbf{a}+\mathbf{b}) \\ EA_2(\mathbf{o}) = \beta A_1(\mathbf{o}) + \beta A_1(-\mathbf{b}) + \beta A_1(-\mathbf{a}-\mathbf{b}) \end{cases}$$

cf. 1D chain

$C(t) = A(x_n)\cdot e^{-\frac{i}{\hbar}Et}$

$A(x_n) = A_o e^{ikx_n}$

Let's take as a trial solution $A_i(\mathbf{r}_n) = A_i e^{i\mathbf{k}\cdot\mathbf{r}_n} (= A_i e^{i(k_x x + k_y y)})$

$$\begin{cases} -EA_1 + (\beta + \beta e^{i\mathbf{k}\cdot\mathbf{b}} + \beta e^{i\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})})A_2 = 0 \\ (\beta + \beta e^{-i\mathbf{k}\cdot\mathbf{b}} + \beta e^{-i\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})})A_1 - EA_2 = 0 \end{cases}$$

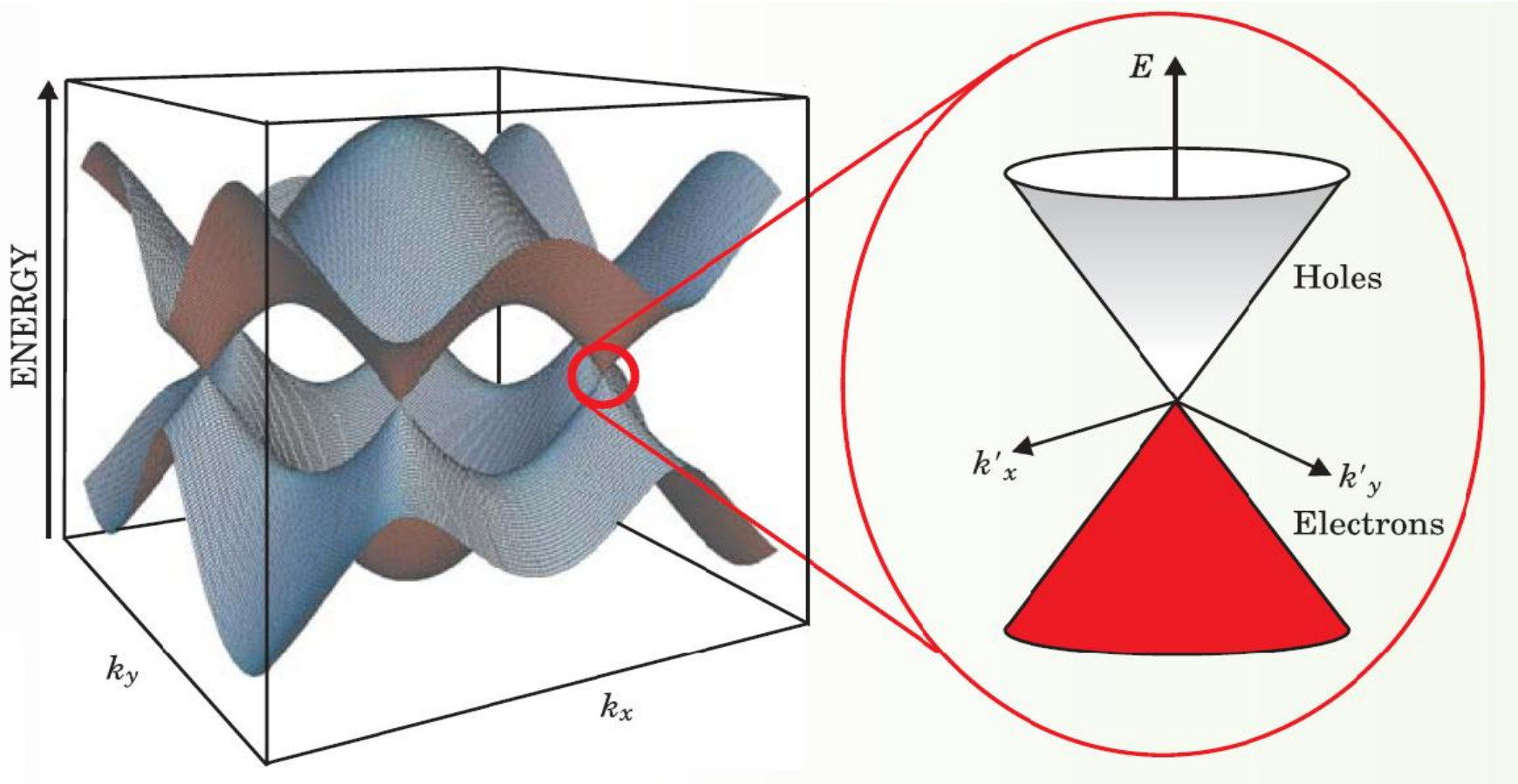
未知数A_1, A_2に対する
連立１次方程式

This is a set of linear algebraic equations for the unknowns A_1 and A_2, and there is a solution if the determinant of the coefficients of A_1 and A_2 is zero.

$$\begin{vmatrix} -E & \beta + \beta e^{i\mathbf{k}\cdot\mathbf{b}} + \beta e^{i\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})} \\ \beta + \beta e^{-i\mathbf{k}\cdot\mathbf{b}} + \beta e^{-i\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})} & -E \end{vmatrix} = 0$$

Dirac cone

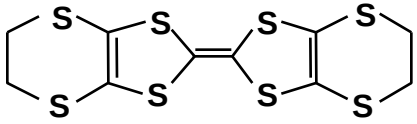
$$E(\mathbf{k}) = \pm|\beta|\sqrt{3 + 2\cos\mathbf{k}\cdot\mathbf{a} + 2\cos\mathbf{k}\cdot\mathbf{b} + 2\cos\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})}$$

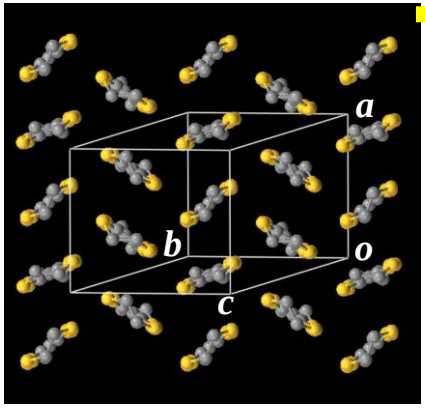


Zero-gap conductor

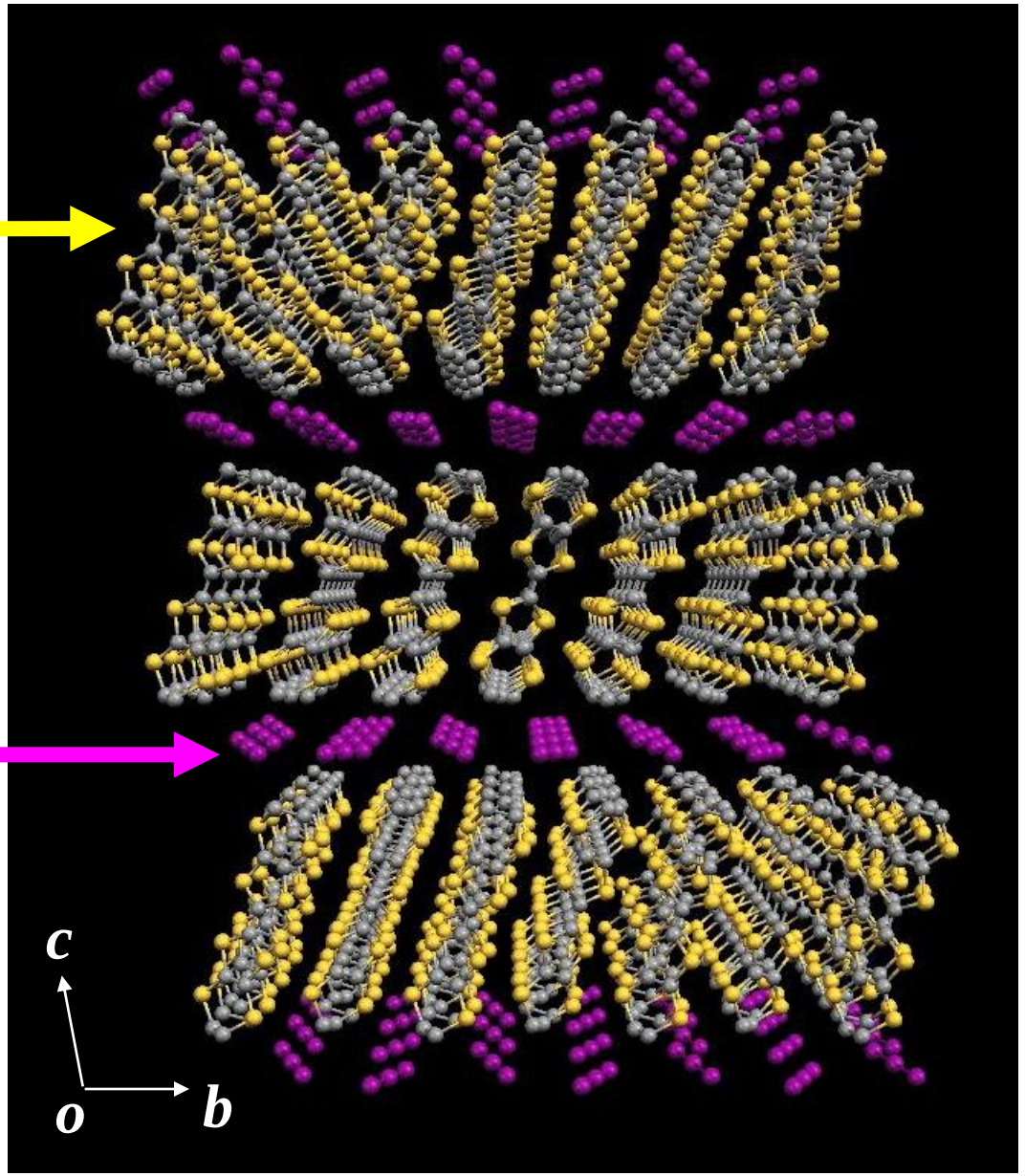
Bulk zero-gap conductor: α-$(ET)_2I_3$

BEDT-TTF (ET)





I_3^-



Dr. N. Tajime
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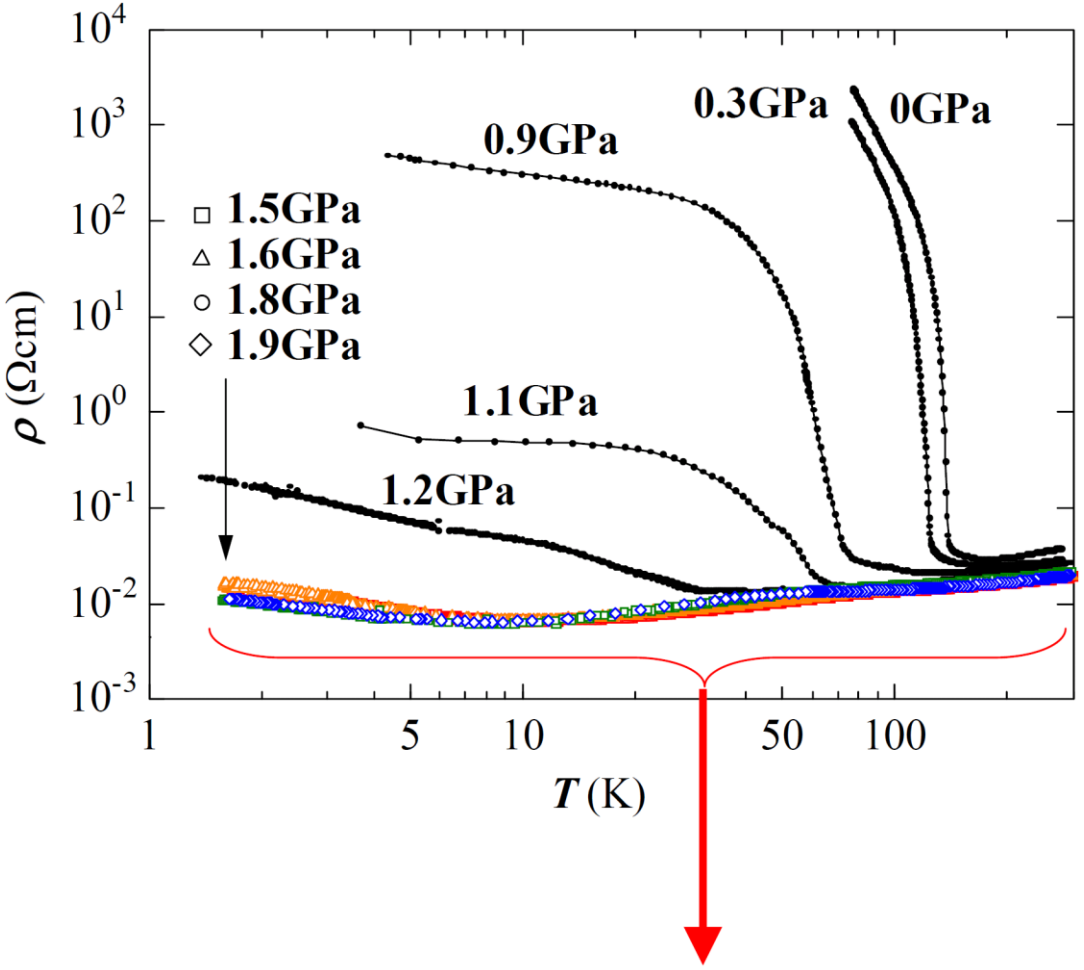
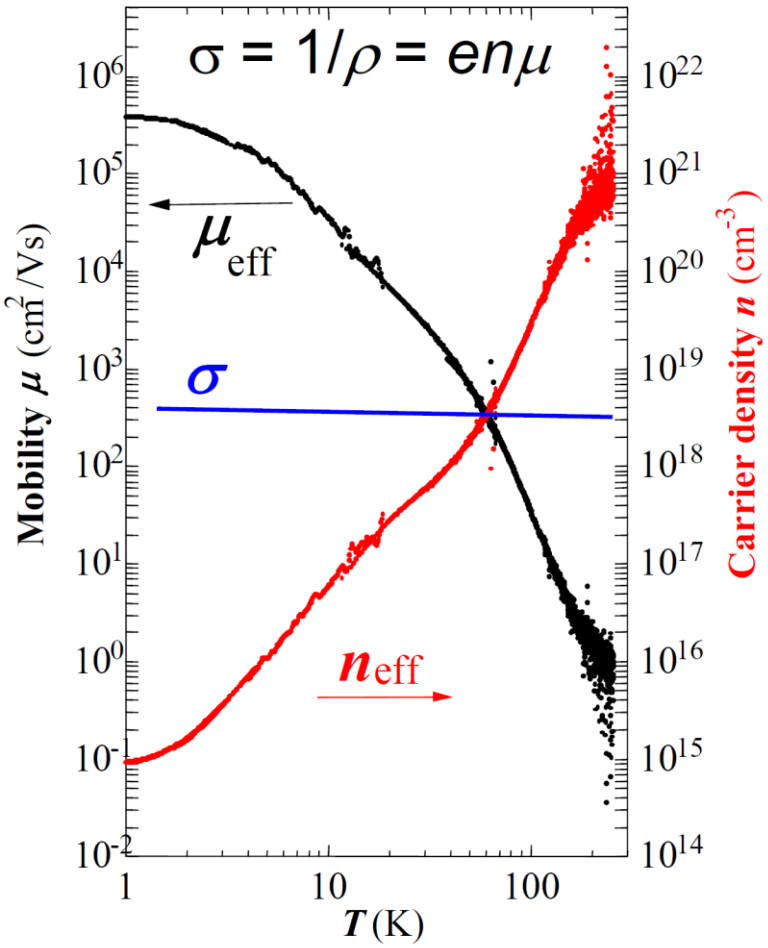
1) *J. Phys. Soc. Jpn.*, **69**, 543 (2000).
2) *Europhys. Lett.* **80**, 47002 (2007).
3) *Phys. Rev. Lett.*, **102**, 176403 (2009).

α-$(ET)_2I_3$: Resistivity under hydrostatic pressure



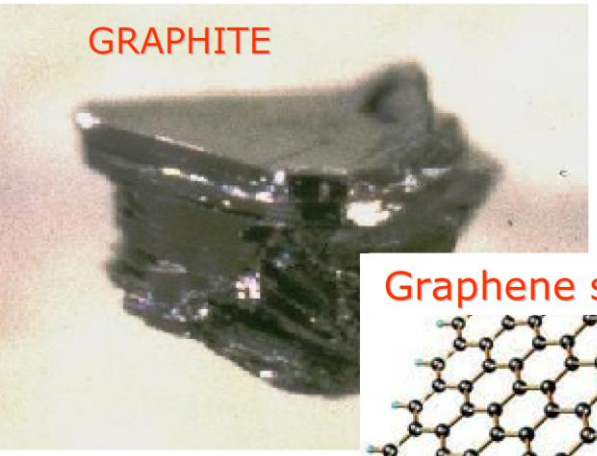
T-independent resistivity

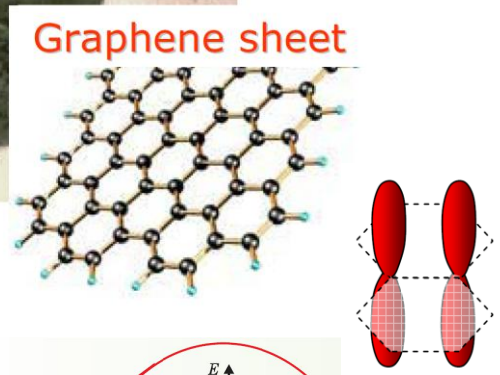


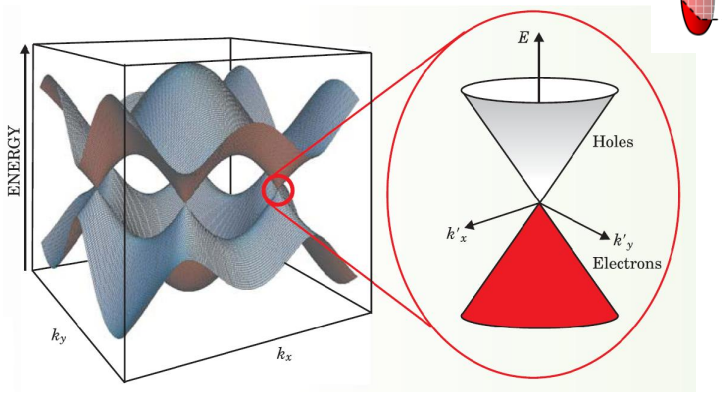
Carrier density and mobility change by about six orders of magnitude, in a manner so that the effects just cancel out.

α-$(ET)_2I_3$ (P >1.5GPa): First bulk zero-gap conductor

Graphene





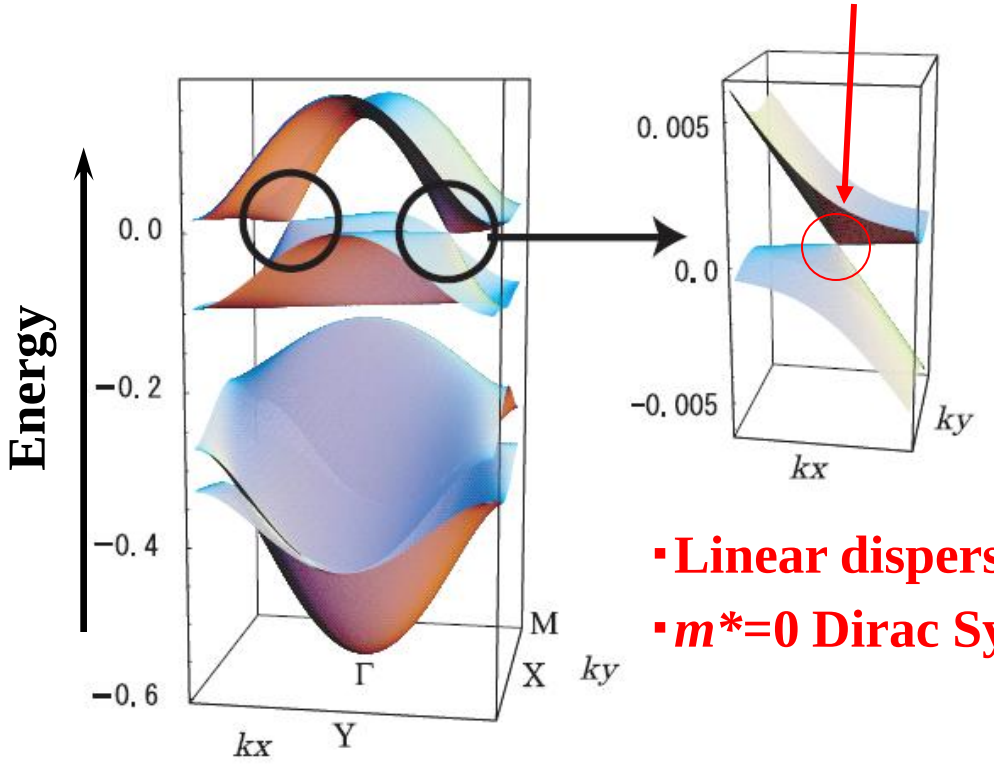


K. S. Novoselov, A. K. Geim et al., *Nature*, **438**, 197 (2005).

Y. Zhang et al., *Nature*, **438**, 201 (2005).

α-$(ET)_2I_3$

Dirac cone

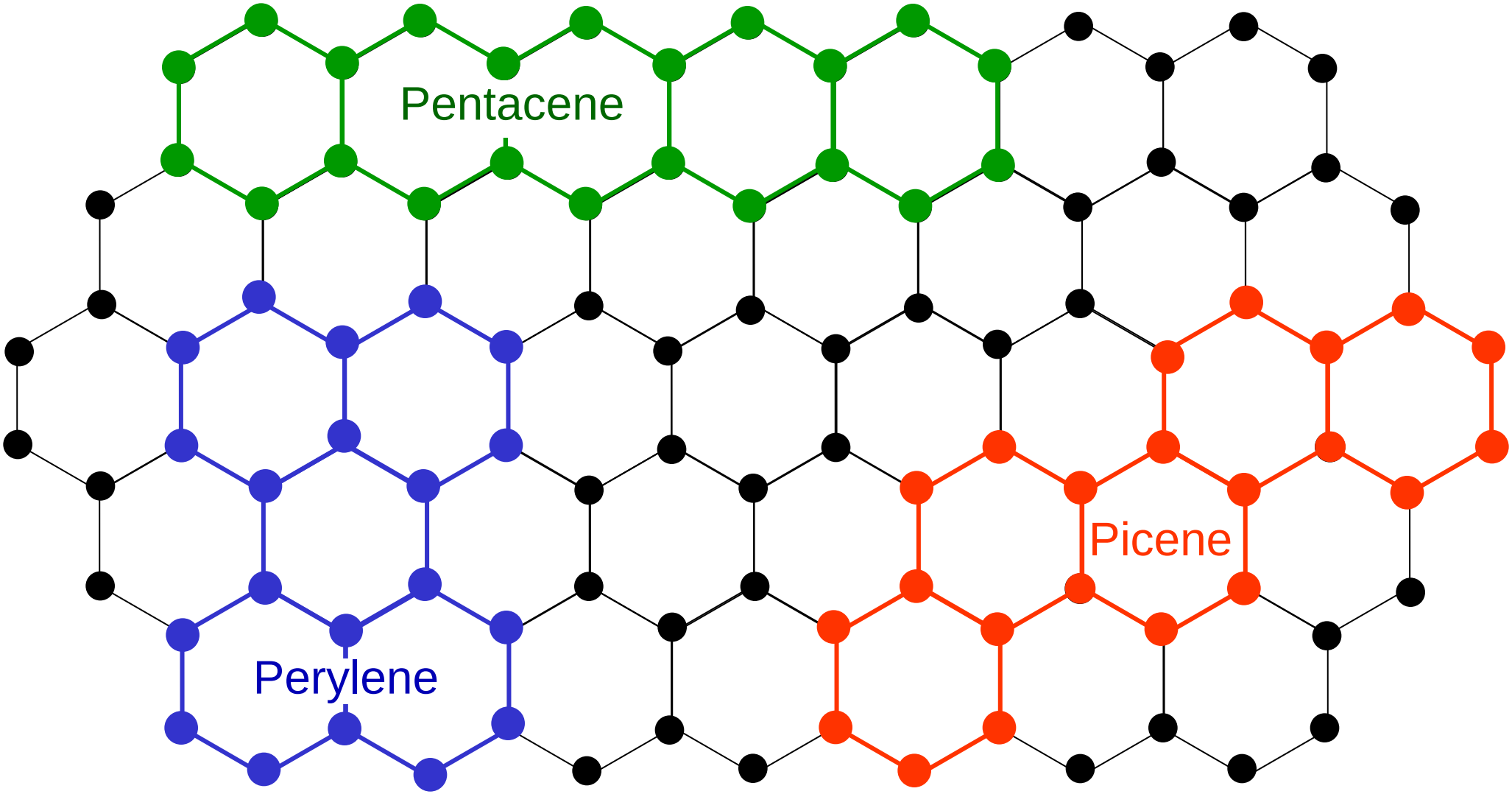


- **Linear dispersion**
- ***m***=0 Dirac System*

Tight-binding model: S. Katayama, A. Kobayashi, and Y. Suzumura, *J. Phys. Soc. Jpn.*, **75**, 054705 (2006).

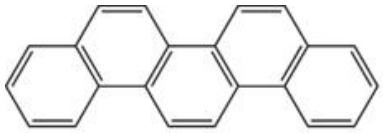
First principle band calculations : H. Kino and T. Miyazaki, *J. Phys. Soc. Jpn.*, **75**, 034704 (2006).

Fragments of graphene



Superconductivity in potassium-doped picene

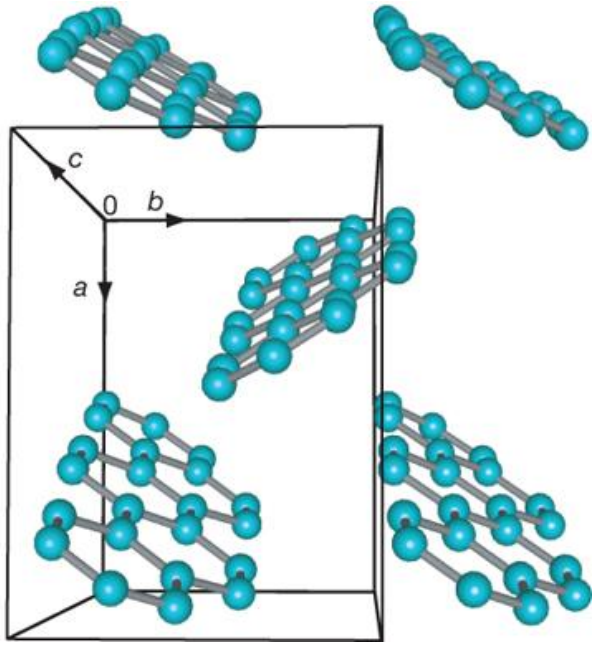
Prof. Y. Kubozono
(Okayama Univ.)

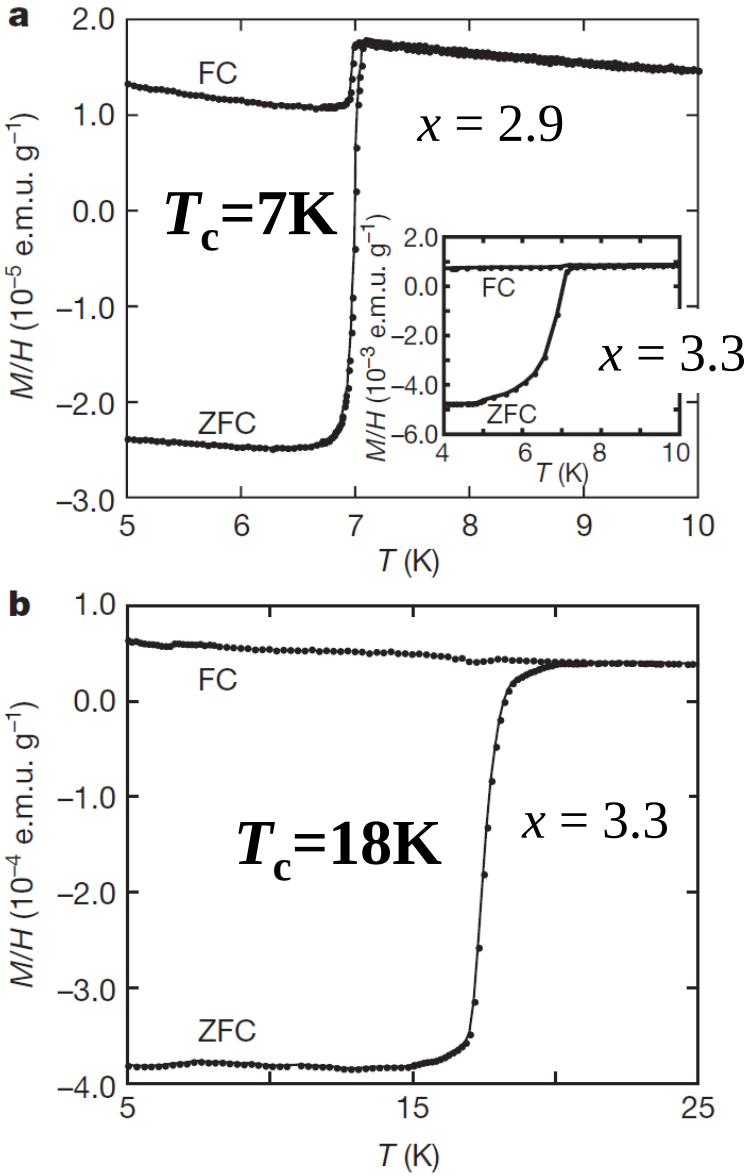


Picene

Picene crystals

$K_x$picene

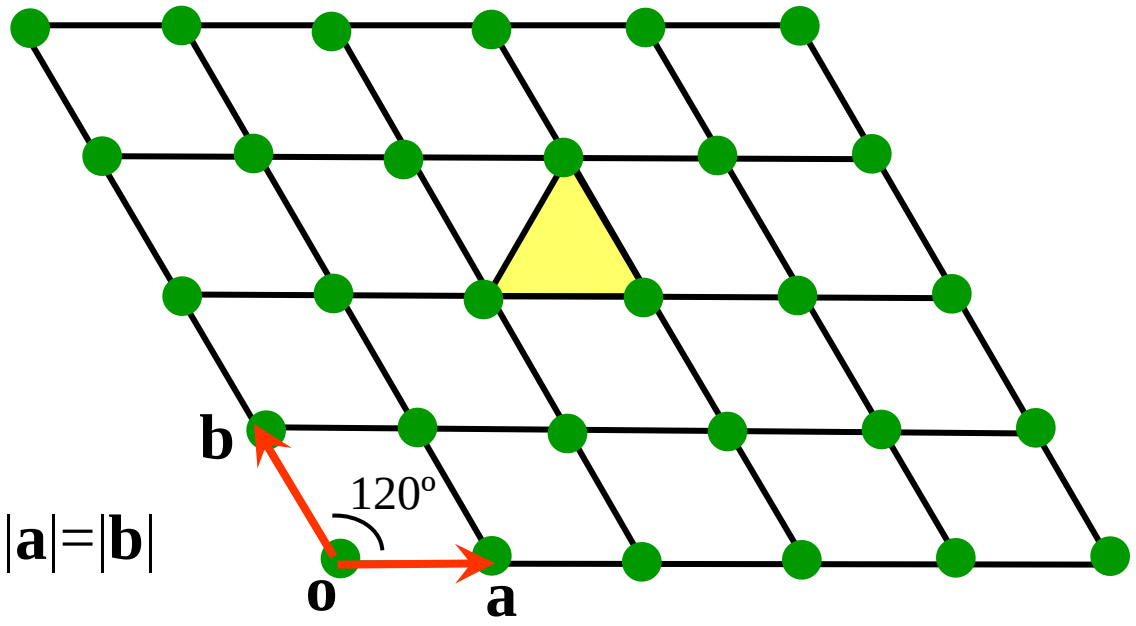




Nature, **464**, 76 (2010)

Triangular lattice

Lattice

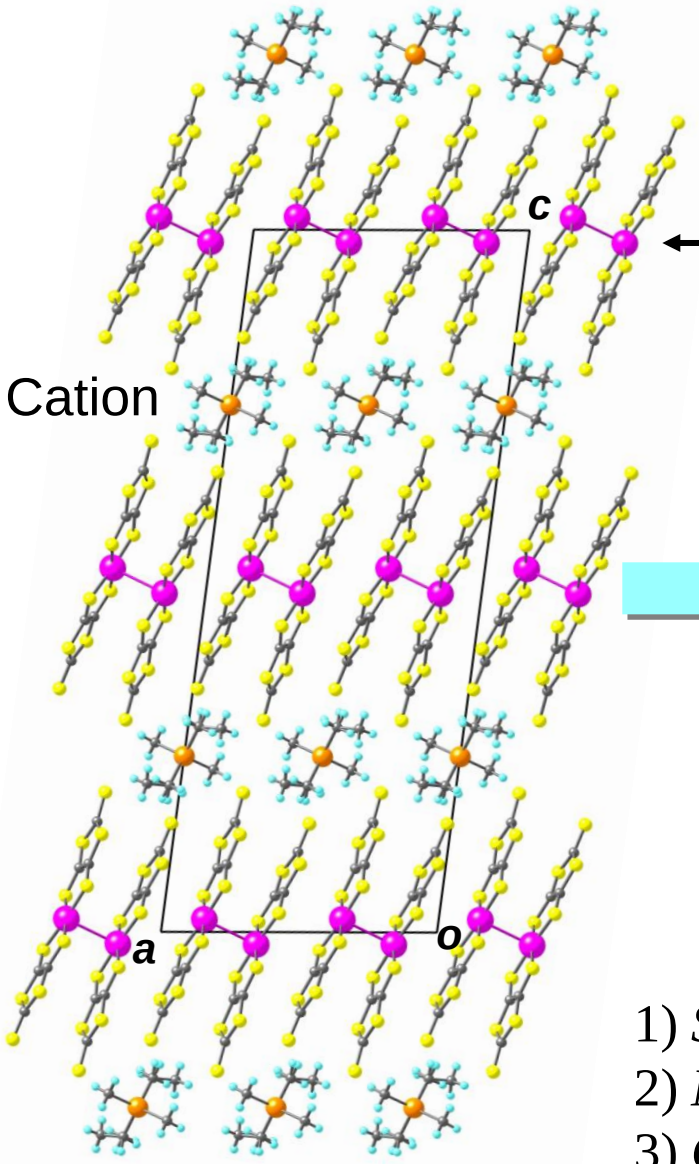


Repeated unit

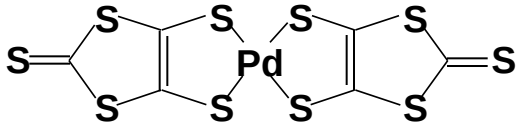
= Triangular lattice

$$E(\mathbf{k}) = \beta\,(2\cos\mathbf{k}\cdot\mathbf{a} + 2\cos\mathbf{k}\cdot\mathbf{b} + 2\cos\mathbf{k}\cdot(\mathbf{a}+\mathbf{b}))$$

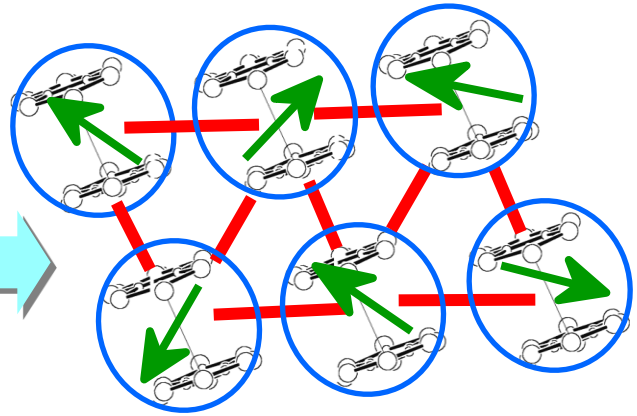
Spin liquid: $EtMe_3Sb[Pd(dmit)_2]_2$



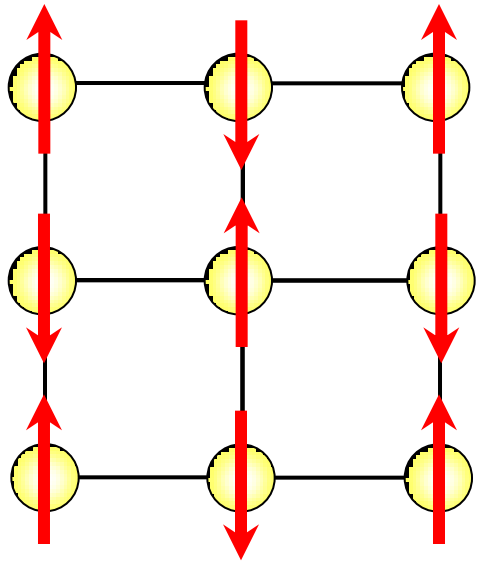
Cation



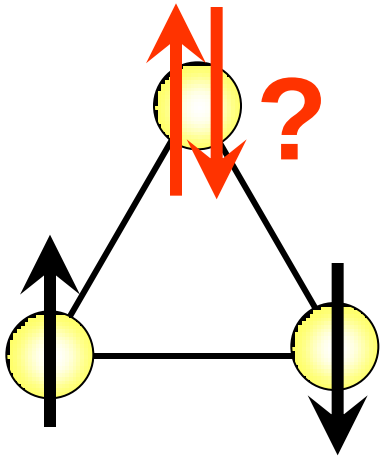
$Pd(dmit)_2$



Triangular lattice of $[Pd(dmit)_2]_2^-$



Square lattice



Spin frustration

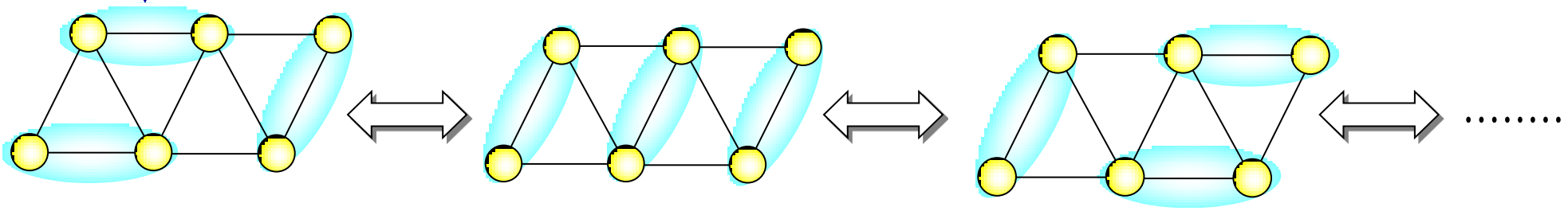
1) *Science*, **328**, 1246 (2010).
2) *Nature Physics*, **6**, 673 (2010).
3) *Chem. Rev.*, **104**, 5319 (2004).

Quantum Spin Liquid (QSL)

- QSL: A spin system in which quantum fluctuations prevent order, leading to liquid-like properties among the spins, even at *zero* temperature.

Singlet spin pair
(Valence Bond)

Resonation between highly degenerated spin configurations leads to a liquid-like wavefunction.



- A long-sought state of matter that has attracted much theoretical attention since its proposal by P. W. Anderson in 1973.

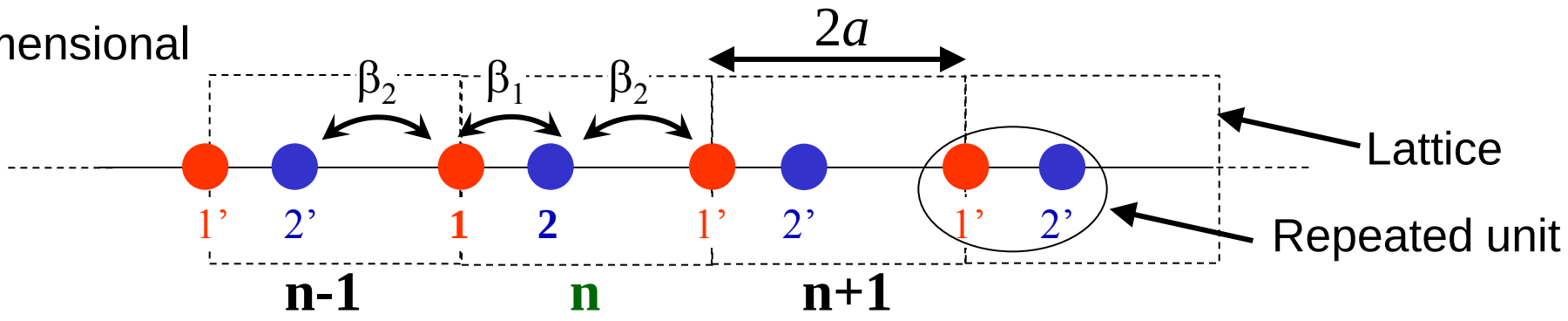
- There are few candidates of the real materials.
(*Two* in the molecular system: κ-$(ET)_2Cu_2(CN)_3$, $EtMe_3Sb[Pd(dmit)_2]_2$)

Summary

1. The electron is the lead of solid state science.
2. The state of the electrons can be represented as a linear combination of a set of base states with suitable coefficients (probability amplitudes).
3. The energy states of the electron can be obtained by the Hamiltonian matrix.
4. Metals are materials that have partially-filled energy bands.
5. Crystals are described by a (Bravais) lattice and a repeated unit.
6. Electronic properties strongly depend on crystal structures.

Appendix: Dimerized chain (I)

One-dimensional crystal



$$\begin{cases} i\hbar \dfrac{dC_{1,\mathrm{n}}}{dt} = \alpha C_{1,\mathrm{n}} + \beta_1 C_{2,\mathrm{n}} + \beta_2 C_{2,\mathrm{n-1}} \\ i\hbar \dfrac{dC_{2,\mathrm{n}}}{dt} = \alpha C_{2,\mathrm{n}} + \beta_1 C_{1,\mathrm{n}} + \beta_2 C_{1,\mathrm{n+1}} \end{cases}$$

In the stationary state, $C_{i,\mathrm{n}}(t) = A_i(\mathrm{n}) \cdot e^{-\frac{i}{\hbar}Et}$

$$\begin{cases} EA_1(\mathrm{n}) = \alpha A_1(\mathrm{n}) + \beta_1 A_2(\mathrm{n}) + \beta_2 A_2(\mathrm{n-1}) \\ EA_2(\mathrm{n}) = \alpha A_2(\mathrm{n}) + \beta_1 A_1(\mathrm{n}) + \beta_2 A_1(\mathrm{n+1}) \end{cases}$$

Dimerized chain (II)

Let's take as a trial solution $A_i(\mathrm{n}) = A_i e^{ik\cdot 2a\mathrm{n}}$

$$\begin{cases} (\alpha - E)A_1 + (\beta_1 + \beta_2 e^{-ik\cdot 2a})A_2 = 0 \\ (\beta_1 + \beta_2 e^{ik\cdot 2a})A_1 + (\alpha - E)A_2 = 0 \end{cases}$$

This is a set of linear algebraic equations for the unknowns A_1 and A_2, and there is a solution if the determinant of the coefficients of A_1 and A_2 is zero.

$$\begin{vmatrix} \alpha - E & \beta_1 + \beta_2 e^{-ik\cdot 2a} \\ \beta_1 + \beta_2 e^{ik\cdot 2a} & \alpha - E \end{vmatrix} = 0$$

$$\therefore E(k) = \alpha \pm \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cdot \cos 2ka}$$

Energy band for a dimerized chain