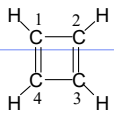


Secular equation of cyclobutadiene in the Huckel model.



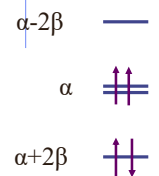
$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & 0 & 0 \\ 0 & 0 & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

From $\begin{vmatrix} A & B \\ B & A \end{vmatrix} = |A+B||A-B|$

The solutions are $E = \alpha, \alpha, \alpha \pm 2\beta$

Bonding energy is $2(\alpha+2\beta) + 2\alpha - 4\alpha = 2 \times 2\beta = 4\beta$

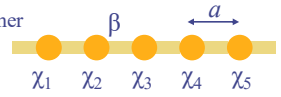
There is no energy gain compared with two double bonds $2 \times 2\beta = 4\beta$



2

Energy Band (Tight-Binding Approximation)

LCAO-MO of a one-dimensional polymer (Hückel MO of polyacetylene)



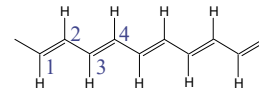
$$\phi = \sum_n c_n \chi_n$$

The secular equation is

$$\begin{vmatrix} \alpha - E & \beta & 0 & \dots \\ \beta & \alpha - E & \beta & \\ 0 & \beta & \alpha - E & \\ \dots & & & \dots \end{vmatrix} = 0$$

$N \times N$

We can directly solve this, but we use another way:



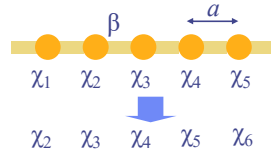
3

$$\phi = \sum_n c_n \chi_n$$

translation by one unit cell, $r \rightarrow r+a$ should not change the physics, because it only changes the atom number. So the electron density $\rho = \phi^* \phi$ does not change. Accordingly, $c_{n+1}^* c_{n+1} = c_n^* c_n$, or only the phase of c_n may change. Thus, we can put $c_{n+1} = c_n e^{i\theta} = c_n e^{ika}$. Consequently ϕ is:

$$\begin{aligned} \phi &= c_0 [\chi_0 + e^{ika} \chi_1 + e^{i2ka} \chi_2 + e^{i3ka} \chi_3 + e^{i4ka} \chi_4 + \dots] \\ &= c_0 \sum_n e^{inka} \chi_n \end{aligned}$$

(Bloch function)
 c_0 is mere a normalization constant.

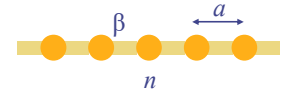


4

Energy of $\phi = \sum_n e^{inka} \chi_n$ is

$$E = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} = \frac{\int (\sum_m e^{-imka} \chi_m^*) H (\sum_n e^{inka} \chi_n) d\tau}{\int (\sum_m e^{-imka} \chi_m^*) (\sum_n e^{inka} \chi_n) d\tau}$$

$$= \frac{\sum_m \sum_n e^{i(n-m)ka} \int \chi_m^* H \chi_n d\tau}{\sum_n \sum_m e^{i(n-m)ka} \int \chi_m^* \chi_n d\tau}$$

$$= \frac{N(e^{ika} \beta + \alpha + e^{-ika} \beta)}{N}$$


$\beta = \int \chi_{n-1}^* H \chi_n d\tau$ $\beta = \int \chi_{n+1}^* H \chi_n d\tau$

$\alpha = \int \chi_n^* H \chi_n d\tau$

$E = \alpha + 2\beta \cos ka$

$\cos ka = \frac{e^{ika} + e^{-ika}}{2}$

5

$E = \alpha + 2\beta \cos ka$

(1) Owing to the periodicity, we only consider $-\pi < ka < \pi$ or $-\pi/a < k < \pi/a$

(2) Owing to $\beta < 0$,
 Maximum of E is (at $k = \pi/a$) $E = \{ \}$
 Minimum of E is (at $k = 0$) $E = \{ \}$

(3) As a whole, the energy band has the bandwidth, $\{ \}$

6

$E = \alpha + 2\beta \cos ka$

$\phi = \sum_n e^{inka} \chi_n$

(4) Make a ring.
 (Otherwise, "edge state" appears.)
 When the total atoms are N , N -th atom = 0-th atom, so
 $e^{iNka} = 1 \rightarrow Nka = 2\pi n$ (n : integer) $\rightarrow k = \{ \}$ Periodical boundary condition

Arranged with a fine interval
 The interval is $\Delta k = \{ \}$
 Very fine for large N .
 \rightarrow Nearly continuous (Energy band)

7

$E = \alpha + 2\beta \cos ka$

(5) $\phi = \sum_n e^{inka} \chi_n$
 $k = 0$ leads to $\phi = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$
 $k = \pi/a$ leads to $\phi = \{ \}$

All intervals have nodes.
 \rightarrow Completely antibonding

Completely bonding

The state next to $k=0$ has extra $e^{i\frac{2\pi}{N}}$ phase. When rotated around the solid, the phase shifts by 2π . So the whole solid has only one node.

8

(6) Total number of levels

$\frac{2 \times \frac{\pi}{a}}{\frac{2\pi}{Na}} = \{ \}$ level interval
 from $-\pi/a$ to π/a
 N atoms $\rightarrow N$ energy levels

(7) For N electrons
 $\frac{2 \times \frac{k_F}{a}}{\frac{2\pi}{Na}} = N \rightarrow k_F = \{ \}$
 for half-filled.

$-\pi/2a$ $k_F = \pi/2a$

Polyacetylene without bond alternation 9

(8) For $2N$ electrons

$$2 \frac{2k_F}{\frac{2\pi}{Na}} = 2N \rightarrow k_F = \left(\right)$$

All states are occupied

Two electrons, \uparrow and \downarrow , enter in one atomic orbital χ .

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(9) For $N=6$

$$k = \frac{2\pi n}{Na} = \frac{2\pi n}{6a} \text{ leads to } E = \alpha + 2\beta \cos ka = \alpha + 2\beta \cos \frac{2\pi}{6} n$$

$0, \pm\pi/3, \pm 2\pi/3, \pi$

$$E = \left(\right) \left(\right) \left(\right) \left(\right) \left(\right) \left(\right)$$

π orbitals (Hückel method) for benzene

Similarly, we can calculate Hückel molecular orbitals for N -carbon rings. 11

Free electron approximation

- (1) Simple free electron approximation derived from the first principle of **quantum mechanics**.
- (2) Electrons in metals, particularly the energy and momentum distribution, are investigated starting from a large number of free electrons.
- (3) Distribution of electrons at finite temperatures are discussed in view of the Fermi statistics: **statistical mechanics**.

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Free electron

$E = \frac{\hbar^2 k^2}{2m}$ parabola

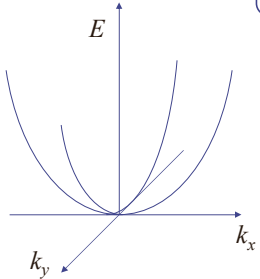
left bound electron $p = -\hbar k$ right bound electron $p = \hbar k$

Wave number $k = 2\pi/\lambda$ is inverse of the wavelength.
The number of waves in unit $\times 2\pi$ length.

13

$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V$ in three dimension.
 Schrödinger equation is,

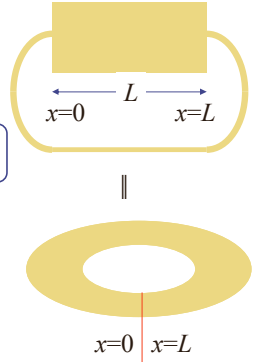
$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\phi = E\phi$$
 Eigenfunction (solution) for $V=0$ is $\phi(x,y,z) = e^{i(k_x x + k_y y + k_z z)}$
 Eigenvalue (energy) is $E = \left[\right]$



We cannot depict k_z at the same time.

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Instead of an infinite space, consider a box with a finite length L , and the $x=L$ edge is connected to $x=0$.
 (Otherwise, the edge generates a "surface" state.)
 $\phi(x+L, y, z) = \phi(x, y, z)$



$e^{ik_x L} = 1 \rightarrow k_x L = 2\pi n \rightarrow k_x = \left[\right]$
 $(n : \text{integer})$

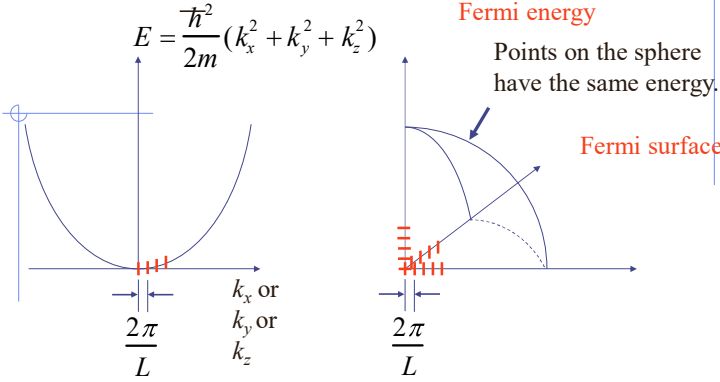
Similarly for y, z ,
 $k_x = \frac{2\pi}{L} n_x \quad k_y = \frac{2\pi}{L} n_y \quad k_z = \frac{2\pi}{L} n_z$

(Consider a cube with L edges.)

Periodical boundary condition

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$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$



Points on the sphere have the same energy.
 Fermi surface

Interval of energy levels
 \rightarrow continuous for large L .
 \rightarrow Energy band

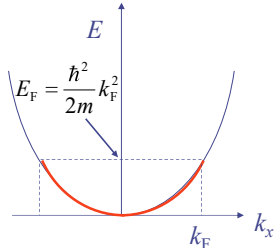
Fill N electrons according to the Pauli's exclusion principle.
 Starting from the origin with the minimum energy, to the inside of a sphere with radius $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$

16

Volume of a sphere with radius k is

$$2 \frac{\frac{4\pi}{3} k^3}{\left(\frac{2\pi}{L}\right)^3} = N \rightarrow \left[\right] = N \text{ where } V = L^3$$

Interval of states (3D) Electron with the highest energy (Fermi energy) is
 One energy level has two electrons with \uparrow and \downarrow spins $k_F^2 = k_x^2 + k_y^2 + k_z^2$



$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} \times \left[\right]$

is solved as for N to give,

$$N = \frac{V}{3\pi^2} \times \left[\right]$$

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Differentiate as for E , and the number of energy levels per unit energy (density of states or states density) is

$$D(E) = \frac{dN}{dE} = \left[\dots \right] \text{ or } D(E) = \frac{3N}{2E}$$

Count energy levels for each energy interval.

$D(E) \propto E^{1/2}$

$D(E)$ is the number of levels in between E and $E+dE$.

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Another derivation of states density

dN is the number of states in between E and $E+dE$.

Surface of the sphere

$$2 \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = dN$$

Interval of the states in 3D

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \left[\dots \right]$$

$$D(E) = \frac{dN}{dE} = 2 \frac{4\pi k^2}{\left(\frac{2\pi}{L}\right)^3} \frac{1}{\hbar^2 k} \frac{1}{m} dk = \frac{V}{2\pi^2} \frac{2m}{\hbar^2} k = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} E^{\frac{1}{2}}$$

$k = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$ The same conclusion

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Two-dimensional metal

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2) = \text{const.} \rightarrow \text{leads to } k_x^2 + k_y^2 = k_F^2 = \text{const.}$$

Occupied Fermi surface = cylinder

Area of the circle

$$2 \frac{\pi k^2}{\left(\frac{2\pi}{L}\right)^2} = N \Rightarrow N = \frac{L^2}{2\pi} k^2 = \left[\dots \right] \Rightarrow D(E) = \frac{dN}{dE} = \left[\dots \right]$$

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Fermi statistics: only one electron can occupy a state.

Occupied by N_i electrons

N_i electrons are in the C_i states with energy E . We cannot distinguish N_i electrons, so that the statistical weight is the number to choose N_i from C_i :

$$W_i = \frac{C_i!}{N_i!(C_i - N_i)!}$$

The definition of entropy in statistical mechanics is

$$S = k_B \ln W = k_B \ln \prod_i W_i = k_B \sum_i \ln W_i = k_B \sum_i \ln \frac{C_i!}{N_i!(C_i - N_i)!}$$

$$= k_B \sum_i (C_i \ln C_i - N_i \ln N_i - (C_i - N_i) \ln (C_i - N_i))$$

Stirling' equation $\ln N! = N \ln N - N$

21

The realized distribution of N_i minimizes the Gibbs free energy
 $F = E - TS - \mu N$ where $E = \sum N_i E_i$, $N = \sum N_i$.

So differentiation of F as for N_i is zero to give,

$$\frac{\partial F}{\partial N_i} = E_i + k_B T (\ln N_i - \ln(C_i - N_i)) - \mu = 0$$

Occupation $f(E_i) = \frac{N_i}{C_i} = \left[\frac{C_i - N_i}{N_i} e^{\frac{E_i - \mu}{k_B T}} \right]$

Fermi-Dirac distribution

When $T=0$:

$$E < \mu \quad f(E) = \frac{1}{e^{-\infty} + 1} = \left[\right]$$

$$E > \mu \quad f(E) = \frac{1}{e^{+\infty} + 1} = \left[\right]$$

$E_F = \mu$: chemical potential

When $T \neq 0$, $f(E)$ changes continuously from 1 to 0 with the width of $k_B T$.

22

The real electron number is $D(E) \times f(E)$

$C_i \times \frac{N_i}{C_i} = N_i$ At $T \neq 0$, these electrons are thermally excited.

$\frac{E_F}{k_B T} \approx \frac{50000 \text{ K}}{300 \text{ K}} > 100 \rightarrow$ Only $< 1\%$ electrons are thermally excited.

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Internal energy of metal electrons

$$U(T) = \int_0^\infty (E - E_F) D(E) f(E) dE$$

Specific heat $C_v = \frac{\partial U}{\partial T} = \int_0^\infty (E - E_F) D(E) \frac{\partial f(E)}{\partial T} dE$

Measured from $E_F = 0$. T appears only in $f(E)$.

where $f(E_i) = \frac{1}{e^{\frac{E_i - \mu}{k_B T}} + 1} = \frac{1}{e^x + 1}$ $x = \frac{E - \mu}{k_B T}$ gives

$$\frac{\partial f}{\partial T} = \left[\right] dx = \frac{dE}{k_B T}$$

$\frac{\partial f(E)}{\partial T}$ is nonzero only near E_F . so that approximated to be $D(E) \sim D(E_F)$.

24

$$C_v = D(E_F) \int_0^\infty (E - E_F) \frac{\partial f(E)}{\partial T} dE$$

$$= D(E_F) \int_0^\infty (k_B T x) \frac{x}{T (e^x + 1)^2} k_B T dx$$

$$= k_B^2 T D(E_F) \int_0^\infty x^2 \frac{e^x}{(e^x + 1)^2} dx \quad \pi^2/3 \text{ from table of integrals}$$

$$= \left[\right] T \quad C_v = \gamma T$$

Specific heat of metal electrons

or using $D(E_F) = \frac{3}{2} \frac{N}{E_F} = \frac{3}{2} \frac{N}{k_B T_F}$ T_F : Fermi temperature

$$C_v = \frac{\pi^2}{3} \frac{3}{2} \frac{N}{k_B T_F} k_B^2 T = \frac{\pi^2}{2} N k_B \frac{T}{T_F} = \frac{\pi^2}{2} n R \frac{T}{T_F}$$

Gas constant

25

If free electron is an ideal gas, according to the Dulong-Petit theorem, the specific heat is $C_v=3R$. However, it is less than

$$\frac{T}{T_F} \approx \frac{300\text{K}}{50000\text{K}} \approx 10^{-2}$$

- Owing to the Fermi distribution, only $k_B T$ electrons near E_F are excited, and contribute to the specific heat.
- Metal electrons are "Fermi" particles!
- Fermi gas cf. Classical gas

At low temperatures (<50 K), the lattice vibration (phonon) decays as $C_v \propto T^3$ so that

$$C_v = \gamma T + \beta T^3 \quad \Rightarrow \quad \frac{C_v}{T} = \gamma + \beta T^2$$

free electron phonon

Experimental estimation of $\gamma \rightarrow D(E_F)$ from the low-temperature (<4 K) specific heat. γ

Bose-Einstein statistics

Insert N_i particles in C_i levels, allowing any particles in the same level.

The number to arrange N_i particles and C_i-1 partitions.

$$W_i = \frac{(C_i + N_i - 1)!}{N_i! (C_i - 1)!}$$

$C_i - 1 \rightarrow C_i$ gives

$$\ln W_i = (C_i + N_i) \ln(C_i + N_i) - N_i \ln N_i - C_i \ln C_i$$

Put this in $F = E - TS - \mu N$, and differentiation as for N_i is put zero to

$$\frac{\partial F}{\partial N_i} = \left[\dots \right] = 0 \quad \Rightarrow \quad \frac{C_i + N_i}{N_i} = e^{\frac{E_i - \mu}{k_B T}}$$

$$f(E_i) = \frac{N_i}{C_i} = \left[\dots \right] \quad \text{Bose-Einstein statistics}$$

$T \rightarrow 0$

$E_i - \mu > 0 \quad e^{+\infty} \rightarrow +\infty \quad f(E) \rightarrow 0$

$E_i - \mu = 0 \quad e^0 \rightarrow 1 \quad f(E) \rightarrow +\infty$

All particles go to the lowest level.

$E_i - \mu \rightarrow \hbar\omega$ gives $f(E_i) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$ Planck distribution

Phonon (lattice vibration) is Bose-Einstein particle.
Photon (light) is the same \rightarrow black body

$$f(E_i) = \frac{1}{e^{\frac{E_i - \mu}{k_B T}} \pm 1} \quad \left\{ \begin{array}{l} + \\ - \end{array} \right.$$

Quantum statistics

$E - \mu \gg k_B T$ leads to $e^{\text{large}} \gg 1 \quad f(E_i) = e^{-\frac{E_i - \mu}{k_B T}}$

Boltzmann (classical) distribution

Classical distribution

Each i -th state has n_i particles, with the total $N = \sum n_i$ particles.

The statistical weight is

$$W = \frac{N!}{n_1! n_2! n_3! \dots}$$

so $\ln W = \ln \frac{N!}{n_1! n_2! n_3! \dots} = N \ln N - \sum_i n_i \ln n_i$ (Stirling's equation)

Put this in $F = E - TS - \mu N \quad (S = k_B \ln W)$

$$F = \sum_i E_i n_i - k_B T (N \ln N - \sum_i n_i \ln n_i) - \mu \sum_i n_i$$

Differentiation as for n_i is zero to give,

$$\frac{\partial \mathcal{F}}{\partial N_i} = \left[\dots \right] = 0$$

so

$$f(E_i) = n_i = \left[\dots \right] \text{ Boltzmann distribution}$$

$$f(E_i) = \frac{1}{e^{\frac{E_i - \mu}{k_b T}} - 1}$$

Bose distribution : Particles with integer spin quantum number :
Light (photon), Lattice vibration (phonon), ^4He

Boltzmann distribution : classical particles

$$f(E_i) = e^{-\frac{E_i - \mu}{k_b T}} \quad f(E_i) = \frac{1}{e^{\frac{E_i - \mu}{k_b T}} + 1}$$

Fermi distribution : Particles with half-integer spin quantum number : electron, proton, neutron, ^3He

Everything approaches to Boltzmann at $E_i - \mu \gg k_b T$.

One-dimensional metal

$$E = \frac{\hbar^2 k_x^2}{2m} = \text{const. leads to } k_x = k_F = \text{const.}$$

(No momentum for k_y, k_z = does not move)

Fermi surface consists of a pair of planes.

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Density of states in one-dimensional metals

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \frac{\sqrt{2mE}}{\hbar}$$

Length of the line \downarrow

$$2 \frac{2k}{2\pi} = N \Rightarrow N = \frac{2L\sqrt{2mE}}{\pi\hbar}$$

$$D(E) = \frac{dN}{dE} = \frac{L\sqrt{2m}}{\pi\hbar\sqrt{E}}$$

32

$E = \alpha + 2\beta \cos ka$

$e^{ika} = x + iy = \cos\theta + i\sin\theta$

Nonbonding

$N=4n$ uses nonbonding level \rightarrow No stabilization

$N=4n + 2$ does not have nonbonding \square stabilization \rightarrow Hückel role

33

