Intro. to Electro-physics The basics of a band theory

Previous

Crystal waves (i.e. phonons) in periodic 1D crystal

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This lecture

Electrons (i.e. electron waves) in periodic 1D crystal



Electrons in 1D crystal

- Orbitals in a 1D crystal = A linear chain of atomic orbitals
 - A single orbital on the n^{th} atom : $|n\rangle$
 - Periodic boundary conditions : $(N + 1)^{th}$ atom = 1^{st} atom
 - All of the orbitals are orthonormal to each other



<Tight-binding chain> One orbital per atom; electrons can hop from one atom to the neighboring atom

$$: \langle m | n \rangle = \delta_{mn}$$

Orbitals in a 1D crystal constructed by a Linear Combination of Atomic Orbitals (LCAO) $\triangleq |\psi\rangle = \sum \phi_n |n\rangle$



<Periodic boundary condition>





Schrödinger's equation (1/3)

- Schrödinger's equation for a 1D crystal $H|\psi\rangle = E|\psi\rangle$
 - Wave function : $|\psi\rangle = \sum \phi_n |n\rangle$ (Linear Combination of Atomic Orbitals)

 $- H|\psi\rangle = E|\psi\rangle \longrightarrow \sum_{m} \langle n|H|m\rangle\phi_{m} = E\phi_{n}$ - The matrix element of the Hamiltonian : $\langle n | H | m \rangle \triangleq H_{nm}$

- The Hamiltonian (i.e., the energy operator)

$$H = K + \sum_{j} V_{j}, \text{ where } \begin{cases} K = \frac{p^{2}}{2m} : \text{ Kinetic ene} \\ V_{j} = V\left(\mathbf{r} - \mathbf{R}_{j}\right) : \text{ Comparison of } \\ \end{bmatrix}$$

where r: The position of the electron, R_i : The position of the *j*-th nucleus

$$(n = 1, 2, 3, \dots, N)$$

(A set of N eigenvalue equations)

$(N \times N \text{ matrix})$

ergy

oulombic potential of the electron due to j^{th} nucleus



Schrödinger's equation (2/3)

• The matrix element of the Hamiltonian

•
$$H|m\rangle = (K + V_m)|m\rangle + \sum_{j \neq m} V_j|m\rangle,$$

where
$$(K + V_m) | m \rangle = \varepsilon_{atomic} | m \rangle$$
 • ε_{atom}

•
$$H_{nm} = \langle n | H | m \rangle = \varepsilon_{atomic} \delta_{nm} + \sum_{j \neq m} \langle n | V_j | m$$

- Meaning of $\langle n | V_j | m \rangle$
 - An electron on m^{th} atom can **hop** onto n^{th} atom *via* the interaction with the j^{th} atom
 - Simplifying assumption: Such a hopping occurs only if *n* and *m* are the nearest neighbor

$$\sum_{j \neq m} \langle n \,|\, V_j \,|\, m \rangle = \begin{cases} V_0, & n = m & \longrightarrow \\ -t, & n = m \pm 1 & \longrightarrow \\ 0, & \text{otherwise} \end{cases}$$



- $K + V_m$: The Hamiltonian if there were only an isolated m^{th} atom
 - ε_{atomic} : Eigen-energy of an electron on the **isolated** m^{th} atom



Coulomb potential due to all the nuclei except the m^{th} one Hopping term

Schrödinger's equation (3/3)

• The Hamiltonian matrix element (contd.)

$$H_{nm} = \langle n | H | m \rangle = \varepsilon_{atomic} \delta_{nm} + \sum_{j \neq m} \langle n | V_j | m \rangle = (\varepsilon_{atomic} + V_0) - t (\delta_{n+1,m} + \delta_{n-1,m})$$

$$H_{nm} = \begin{pmatrix} \varepsilon_0 & -t & 0 & \cdots & 0 \\ -t & \varepsilon_0 & -t & \cdots & 0 \\ 0 & -t & \varepsilon_0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & -t & \varepsilon_0 \end{pmatrix}$$

- Let $\varepsilon_0 \triangleq \varepsilon_{atomic} + V_0$: Kinetic energy + Coulomb potential due to all the nuclei
- *t* :
- Magnitude of t depends on how close together the adjacent orbitals are

$$\sum_{j \neq m} \langle n \,|\, V_j \,|\, m \rangle = \begin{cases} V_0, & n = \\ -t, & n = \\ 0, & \text{othe} \end{cases}$$

the hopping energy that allows for an electron to move from one site to another site



Solution to Schrödinger's equation

Results of tight-binding model in 1D ullet

• Proposed coefficient : $\phi_n = \frac{e^{-jkna}}{\sqrt{N}}$ (for time-independent S.E \rightarrow no ω term!)

The substitution into the Schrödinger's equation :

$$\sum_{m} H_{nm} \phi_{m} = E \phi_{n} \longrightarrow \begin{cases} (\text{I.h.s.}) \frac{1}{\sqrt{N}} \left[\varepsilon_{0} e^{-jkna} - t \left(e^{-jk(n+1)a} + e^{-jk(n-1)a} \right) \right] \\ (\text{r.h.s}) \frac{1}{\sqrt{N}} E e^{-jkna} \end{cases}$$

- **Dispersion relation :** $E = \varepsilon_0 2t \cos(ka)$
 - Periodic in $k \rightarrow k + 2\pi/a$
 - Periodic boundary conditions with N unit cells $\rightarrow \Delta k = 2\pi/L$ (* N unit cells $\rightarrow N$ allowed k-values)

The matrix element
$$H_{nm} = \varepsilon_0 - t \left(\delta_{n+1,m} + \right)$$



Dispersion relation for a 1D crystal



- Important characteristics
 - Allowed k value : quantized in units of $\Delta k = 2\pi/L$ (c.f., continuous for free electrons)
 - Energy band : The "finite" energy range where the electrons can be populated
 - **Bandwidth** (4t) determined by the magnitude of hopping (or the **interatomic distance**)

Characteristics of band structure (1/2)

- Energy band
 - Hopping (*t*) splits the *N* electronic states into some **higher** energy states and some **lower** energy states with respect to ε_0
 - Splitting becomes intense as interatomic spacing decreases
- Total energy of all of the electrons
 - Average energy of all N states : ε_0
 - If the band is completely filled : $E = N \varepsilon_0$
 - If the band is not filled : $E < N\varepsilon_0$
 - (:: Some of the higher energy states not filled)
 - $E N\varepsilon_0 \triangleq \Delta E$: Binding energy of the crystal

Characteristics of band structure (2/2)

- Dispersion relation near the bottom of the band $E(k) = \varepsilon_0 - 2t \cos(ka) \rightarrow E(k) \approx ta^2k^2 + C$
 - (:: Expanded for small $k \sim 0$)
 - Effective mass

$$E(k) = ta^{2}k^{2} + C = \frac{\hbar^{2}k^{2}}{2m^{*}} + C$$

- The dispersion near the bottom of the band =

The dispersion of free particles with effective mass m^*

Taylor series

$$f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f'''(a)}{3!}(x-a)^3 + \cdots$$

Electrons filling a band

- Monovalent atomic crystal
 - Each atom donates "one" electron into the band
 - The crystal consists of N atoms (or unit cells)

 $\rightarrow N$ possible k-values

- Half-filled band : Due to "two" possible spin states for electrons, only N/2 *k*-values can be occupied
- Only a small amount of energy (e.g. E-field) needed to shift the Fermi surface and move electrons \rightarrow An electric current induced!
- Such a monovalent atomic crystals are mostly metallic!
- Divalent atomic crystal
 - Completely filled band : no response of the electrons upon the application of an E-field \rightarrow No electric current!
 - Such a divalent atomic crystals are mostly insulators!

Metal-to-insulator transition

Previous tight-binding model

One atom per unit cell

One orbital per atom

Monatomic, Divalent

One atom per unit cell

Two orbitals per atom

 \approx

Realistically

One atom per unit cell

Several orbitals per atom (e.g., s, p, d, f, …)

Diatomic, monovalent

Two different atoms per unit cell

One orbital per atom

Interatomic distance (a)

Energy gap (From diatomic crystal vibrations)

Two modes per k value

- Above is when $\kappa_1 \neq \kappa_2$ and $\kappa_1 < \kappa_2$ ullet
- The case of $\kappa_1 = \kappa_2$ •
 - A simple monatomic chain with a lattice constant a/2-

The 1st Brillouin zone :
$$\left[-\frac{2\pi}{a}, \frac{2\pi}{a}\right]$$

One mode per k value

- When the two atoms are only slightly different \bullet
 - A small perturbation applied to a situation where all atoms are identical
 - Due to the perturbation, a small energy gap opens up at the zone boundary, but the rest of the dispersion mostly looks alike that of the monatomic chain!

Energy gap (From electronic band)

- Two different atoms per unit cell

 - Energy gap —

 - (i.e., where the Fermi surface is)

