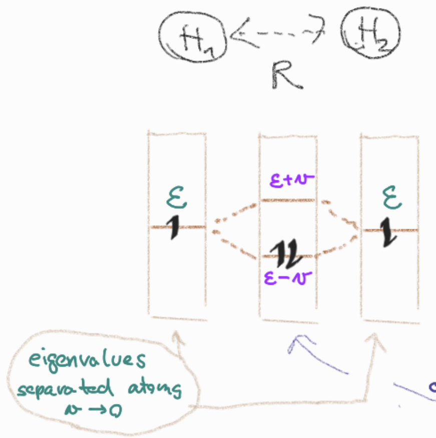
# Tight-binding model (and its applications)

## MOTIVATION

(a) LCAO method in electronic structure of molecules

↳ Linear Combination of Atomic Orbitals

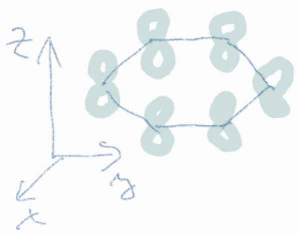
- Example .. simplistic model of covalent bond




- approximation of state space $\mathcal{H}$ by one 1s orbital at each H-atom ... $|\phi_1\rangle, |\phi_2\rangle$
- isolated atom energy:
  $\varepsilon = \langle\phi_1|\hat{H}|\phi_1\rangle + \langle\phi_2|\hat{H}|\phi_2\rangle$
- interaction $v = \langle\phi_1|H|\phi_2\rangle = \langle\phi_2|H|\phi_1\rangle$
  $v \to 0$ for $R\to\infty$ BOND $v\in\mathbb{R}$ (phase convention)
- Hamiltonian eigenvalues: $\begin{pmatrix}\varepsilon & v\\ v & \varepsilon\end{pmatrix}$. $\begin{pmatrix}1\\1\end{pmatrix}$. $\begin{pmatrix}1\\-1\end{pmatrix}$
  $(\varepsilon+v)$ $(\varepsilon-v)$

covalent bounding energy for 2 electrons $2\varepsilon - 2(\varepsilon-v) = 2v$

- Another examples:
  - atomic chain: ... Au (-3) Au (-2) Au (-1) Au (0) Au (1) Au (2) Au (3) ...
  - Hückel model for unsaturated hydrocarbons




... one $p_z$ orbital per carbon atom

↖ for example benzene $H = \begin{pmatrix}\varepsilon & v & 0 & 0 & 0 & v\\ v & \varepsilon & v & 0 & 0 & 0\\ 0 & v & \varepsilon & v & 0 & 0\\ 0 & 0 & v & \varepsilon & v & 0\\ 0 & 0 & 0 & v & \varepsilon & v\\ v & 0 & 0 & 0 & v & \varepsilon\end{pmatrix}$

  - massless Dirac fermions in graphene (later)
  - Quantum dots

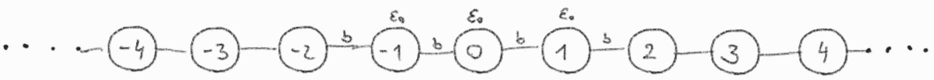
(b) Discretization of Schrödinger eq. $-\frac{\hbar^2}{2m}\psi''(x) = E\psi$

on Lattice $x_n = \Delta\cdot n$ ... $\psi''(x_n) \approx \frac{1}{\Delta^2}(\psi_{n+1} - 2\psi_n + \psi_{n-1})$

$$\to \frac{\hbar^2}{m\Delta^2}\psi_n - \frac{\hbar^2}{2m\Delta^2}(\psi_{n+1}+\psi_{n-1}) = E\psi_n \qquad \hat{H} = \frac{\hbar^2}{2m\Delta^2}\begin{pmatrix}\ddots & \ddots & & & 0\\ \ddots & 2 & -1 & & \\ & -1 & 2 & -1 & \\ & & -1 & 2 & \ddots\\ 0 & & & \ddots & \ddots\end{pmatrix}$$

# A. INFINITE HOMOGENEOUS CHAIN

NEAREST NEIGHBOR TIGHT-BINDING MODEL




particle can hop among Q-dots

- Hilbert space $\equiv \operatorname{span}\{|n\rangle\}_{n=-\infty}^{\infty}$ .. localized basis $|n\rangle \equiv$ site $n$

  NORMALIZATION $\langle n|m\rangle = \delta_{nm}$ COMPLETENESS $\sum_n |n\rangle\langle n| = \hat{I}$

- Translation operator $\hat{\tau}$

  defined by action on basis $\hat{\tau}|n\rangle = |n+1\rangle$ ie. $\hat{\tau} = \sum_n |n+1\rangle\langle n|$

  properties: - UNITARITY: $\hat{\tau}^{+} = \sum_n |n\rangle\langle n+1| = \sum_n |n-1\rangle\langle n|$ ← (proof by subst. $n = n-1$)

  i.e. $\hat{\tau}\hat{\tau}^{+} = \hat{\tau}^{+}\hat{\tau} = \sum_n |n\rangle\langle n| = \hat{I}$

  - spetrum: def $|\varkappa\rangle \equiv \sum_n e^{i\varkappa n}|n\rangle$

  observe $\tau|\varkappa\rangle = \sum_n e^{i\varkappa n}|n+1\rangle = e^{-i\varkappa}\sum_n e^{i\varkappa n}|n\rangle = e^{-i\varkappa}|\varkappa\rangle$

  i.e. $|\varkappa\rangle$ is eigenvector for eigenvalue $\lambda = e^{-i\varkappa}$

  complete set for $\varkappa \in \langle 0, 2\pi)$ ... $\varkappa \to \varkappa + 2\pi$ gives identical vector $|\varkappa\rangle$

  or $\langle -\pi, \pi)$

- dynamics generated by HAMILTONIAN:

$$\hat{H} = \sum_n \varepsilon_0 |n\rangle\langle n| - b\sum_n \left(|n\rangle\langle n+1| + |n+1\rangle\langle n|\right) = \varepsilon_0 \hat{I} - b(\hat{\tau}^{+} + \hat{\tau})$$

on-site energy $\varepsilon_0 = \langle n|H|n\rangle$ hopping amplitude $b = -\langle n|H|n+1\rangle$

hamiltonian is the funcion of $\hat{\tau}$: $\hat{H} = f(\hat{\tau})$ ; $f(x) = \varepsilon_0 - b\left(x + \frac{1}{x}\right)$

→ EIGENVALUES are the same function of $e^{-i\varkappa}$

$E(\varkappa) = \varepsilon_0 - b(e^{i\varkappa} + e^{-i\varkappa}) = \varepsilon_0 - 2b\cos\varkappa$

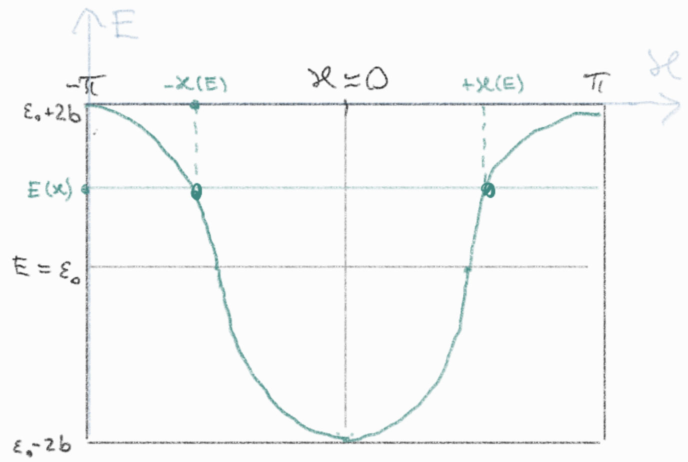
- spectrum of $H$: $\sigma_H = \langle \varepsilon_0 - 2b, \varepsilon_0 + 2b\rangle$

  -- band spetrum of periodic lattice

each value $E \in \langle \varepsilon_0 - 2b, \varepsilon_0 + 2b\rangle$ is 2x degenerate

eigenstates: $|E, \pm\rangle = |\pm\varkappa\rangle$

with $\varkappa(E) = \cos^{-1}\frac{E - \varepsilon_0}{2b}$




Normalization to δ-function

we start with $\langle \varkappa|\varkappa'\rangle = \delta(\varkappa - \varkappa')$ for $|\varkappa\rangle = \eta\sum_n e^{i\varkappa n}|n\rangle$

it is $\langle \varkappa|\varkappa'\rangle = |\eta|^2 \sum_n e^{-i\varkappa n}\langle n|\sum_{n'}|n'\rangle e^{i\varkappa' n'} = |\eta|^2\sum_{nn'} e^{i(\varkappa' n' - \varkappa n)}\delta_{nn'}$

$$= |\eta|^2 \sum_n e^{in(\varkappa' - \varkappa)} = 2\pi|\eta|^2 Ш_{2\pi}(\varkappa' - \varkappa) = 2\pi|\eta|^2\delta(\varkappa' - \varkappa)$$

limited to $\varkappa \in \langle -\pi, \pi)$

## SIDENOTE: Dirac comb $Ш_T(k)$

def: $Ш_T(k) \equiv \sum_{\ell=-\infty}^{\infty} \delta(k-\ell T)$ is periodic extension of $\delta$-function

- most natural for $T=2\pi$ can be understood as single $\delta$-function at angle $k=0$ on circle $k \in \langle 0, 2\pi)$
- its Fourier series coef. is constant sequence $c_m = \frac{1}{T}$
  $\longrightarrow Ш_T(k) = \frac{1}{T} \sum_m \exp\{2\pi i m \frac{k}{T}\}$
- the formula is related to Dirichlet kernel (see wiki)

- used above: $\sum_m e^{imk} = 2\pi\, Ш_{2\pi}(k) = 2\pi \sum_\ell \delta(k-2\pi\ell)$
- natural comb $T=1$: $Ш(k) = \sum_\ell \delta(k-\ell) = \sum_m e^{2\pi i m k}$

i.e. we have normalized states $|\varkappa\rangle = \frac{1}{\sqrt{2\pi}} \sum_m e^{i\varkappa m} |m\rangle$

$\langle \varkappa | \varkappa' \rangle = \delta(\varkappa - \varkappa')$, $\hat{I} = \int_{-\pi}^{\pi} |\varkappa\rangle\langle\varkappa|$

and by substitution theorem in $\delta$-distribution

$$\delta(E-E') = \left|\frac{dE}{d\varkappa}\right|^{-1} \delta(\varkappa-\varkappa') = \frac{\delta(\varkappa-\varkappa')}{|2b\sin\varkappa|}$$

i.e. $\boxed{|E,s\rangle = \frac{1}{\sqrt{|4\pi b \sin\varkappa|}} \sum_m e^{ims\varkappa(E)} |m\rangle}$

- $\langle E, s | E', s' \rangle = \delta_{ss'} \delta(E-E')$ ORTHOGONALITY
- $\hat{I} = \sum_s \int_{\varepsilon_0-2b}^{\varepsilon_0+2b} |E,s\rangle\langle E,s|\, dE$ COMPLETENESS

## • OTHER INTERESTING OBSERVABLES:

– **position**: $\hat{N} = \sum_m m |m\rangle\langle m|$ ... eigenvalues $m \in \mathbb{Z}$

assuming separation of sites $= a$ : $\hat{X} = a\hat{N} = \sum_n x_n |n\rangle\langle n|$

i.e. $|m\rangle$ is eigenvector with position $x_m = am$

NOTE: position operator in $\varkappa$-basis .. $\boxed{\hat{N} = i\frac{d}{d\varkappa}}$

proof: $\hat{N}|\psi\rangle = \sum_m m|m\rangle\langle m| \int_{-\pi}^{\pi} d\varkappa\, \psi(\varkappa)|\varkappa\rangle = \sum_m \int d\varkappa\, |m\rangle \psi(\varkappa) \frac{1}{\sqrt{2\pi}} \underbrace{m e^{i\varkappa m}}_{\frac{1}{i}\frac{d}{d\varkappa} e^{i\varkappa m}} \underset{\text{per partes}}{=} \sum_m |m\rangle \int d\varkappa\, i\psi'(\varkappa)\langle m|\varkappa\rangle = \int d\varkappa \left(i\frac{d}{d\varkappa}\psi(\varkappa)\right)|\varkappa\rangle$

– **velocity**: operator of rate of change of $\hat{X}$ (general concept):

$\forall |\psi\rangle$: $\langle\psi|\hat{v}|\psi\rangle = \frac{d}{dt}\langle\psi|\hat{X}|\psi\rangle = \frac{1}{i\hbar}\langle\psi|\hat{X}\hat{H} - \hat{H}\hat{X}|\psi\rangle$ Schrödinger $\frac{d}{dt}|\psi\rangle = H|\psi\rangle / i\hbar$

i.e. $\hat{v} = \frac{1}{i\hbar}[\hat{X}, \hat{H}] = \frac{-ab}{i\hbar}[\hat{N}, \tau + \tau^+] = \frac{ab}{i\hbar}(\hat{\tau}^+ - \tau) = v_F \frac{\tau^+ - \tau}{2i}$ $\quad v_F \equiv \frac{2ab}{\hbar}$ Fermi velocity

$[\hat{N}, \hat{\tau}] = \sum_n \sum_m m \left(|m\rangle\langle m|m+1\rangle\langle m| - |m+1\rangle\langle m|m\rangle\langle m|\right) = \sum_m (m+1-m)|m+1\rangle\langle m| = \tau$

i.e. eigenvectors are $|\varkappa\rangle$ and eigenvalues $v(\varkappa) = v_F \sin(\varkappa) = \frac{dE(k)}{dk}$

NOTICE: if we introduce momentum (Bloch vector) $k = \varkappa \cdot \frac{\hbar}{a}$ then

## • LONG-WAVELENGTH LIMIT and EFFECTIVE MASS

the stationary-state wave functions $e^{i\varkappa n}$ have the form of plane wave $e^{ikx}$ with

position $\boxed{x_n = an}$; wave-vector $k = \frac{1}{\hbar}p = \frac{2\pi}{\lambda}$ and momentum $\boxed{p = \frac{\varkappa\hbar}{a}}$

consider energy eigenstates for $\varkappa \ll 1$ i.e $\lambda \gg a$ (lattice not resolved)

→ then $E = \varepsilon_0 - 2b\cos\varkappa \simeq \underbrace{\varepsilon_0 - 2b}_{E_0} + 2b\,\frac{1}{2}\varkappa^2 = E_0 + \frac{p^2}{2m^*} = E$ $\qquad \boxed{m^* = \frac{\hbar^2}{2ba^2}}$

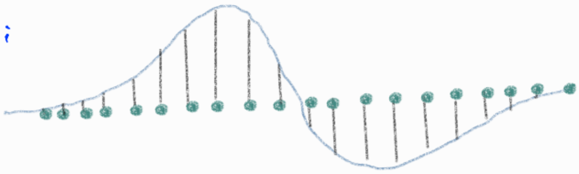
↳ $b p^2 \cdot \left(\frac{a}{\hbar}\right)^2 = p^2 \frac{ba^2}{\hbar^2}$ $\qquad$ EFFECTIVE MASS

→ consistent with velocity $v(\varkappa) = \frac{2ab}{\hbar}\sin\varkappa \simeq \frac{2ab}{\hbar}\varkappa = \frac{p}{m^*}$

CONCLUSION: particle wave-packet on latice:

smoth fontion of x gives Fourier components with $k \ll \frac{\pi}{a}$

⇒ energy i.e. Hamiltonian i.e time-evolution behaves as free particle with mass $m^*$



note: compare discretized Schrödinger equation above $a \equiv \Delta$

$\varepsilon_0 = \frac{\hbar^2}{m\Delta^2}$ $\quad b = \frac{\hbar^2}{2m\Delta^2}$ $\quad \Rightarrow m^* = m$ ✓

## • NOTES ON MANY-PARTICLE ASPECTS

- the chain can be considered empty (empty quantum dots) occupied with one particle only, it is then natural to consider states close to ground state $E = \varepsilon_0 - 2b$
- for atomic chains with alcaline metals it is natural to consider "half-filled chain" with all states with $E \in \langle \varepsilon_0 - 2b, \varepsilon_0 \rangle$ doubly occupied with two electrons with spin up and down.
- total energy is then given by sum of one-particle energies for all occupied states. Proper way to add these requires finite size of chain. Note that we neglected electron-electron interaction.

# B. MODIFICATIONS OF INFINITE HOMOGENEOUS CHAIN

We can look on possible modifications of the model:

- chain with defect
- half chain, finite section, circle and junctions
- periodic chain (SSH model)

## • INFINITE CHAIN WITH DEFECT


Consider the same system as above but with $\langle 0|H|0\rangle = \varepsilon_d = \varepsilon_0 + \sigma$, ie

$$\hat{H} = \sum_m \varepsilon_0 |m\rangle\langle m| - b\sum_m \left(|m\rangle\langle m+1| + |m+1\rangle\langle m|\right) + \sigma|0\rangle\langle 0|$$

We try to find stationary states $|\psi\rangle = \sum_m \psi_m |m\rangle$ solving Schrödinger eq.

$H|\psi\rangle = E|\psi\rangle$ .. projected on $\langle m|$: $\to$ $\boxed{m \neq 0:}$ $\quad \varepsilon_0\psi_m - b(\psi_{m+1} + \psi_{m-1}) = E\psi_m \quad (1)$

$\to$ $\boxed{m = 0:}$ $\quad (\varepsilon_0 + \sigma)\psi_0 - b(\psi_1 + \psi_{-1}) = E\psi_0 \quad (2)$

### • CONTINUOUS SPECTRUM:

Equation (1), i.e. Schrödinger eq. away from the defect is identical to previous case i.e. $\psi_m = e^{i\theta m}$ solves it for energy inside alowed band $E = \varepsilon_0 - 2b\cos\theta \in \langle \varepsilon_0 - 2b, \varepsilon_0 + 2b\rangle$, in fact there are two independent solutions for given E:

$$\left.\begin{aligned} m>0: \quad & \psi_m^{(L)} = A_+ e^{i\theta m} + A_- e^{-i\theta m} \\ m<0: \quad & \psi_m^{(R)} = B_+ e^{i\theta m} + B_- e^{-i\theta m} \end{aligned}\right\}$$

guarantee fulfiling (1)

.. four unknown constants $A_\pm$, $B_\pm$

These functions solve schrödinger equation everywhere except $m = 0, \pm 1$. For $m = \pm 1$ eq (1) requires $\psi_0 = A_+ + A_- = B_+ + B_- = \psi_0$ because (1) is satisfied only if the same form of wavefunction is continued on site $m=0$. The last equation is (2), ie

$$(\varepsilon_0 + \sigma)\psi_0 - b(A_+ e^{i\theta} + A_- e^{-i\theta} + B_+ e^{-i\theta} + B_- e^{i\theta}) = E\psi_0$$

We therefore see that only 2 of four constants are independent, ie two independent solutions for each E. These could be chosen as:

$A_+ = 1,\ B_- = 0$ scattering of particle coming from left

reflection probability $P_R = |A_-|^2$ transmission $P_T = |B_+|^2$

$A_+ = 0,\ B_- = 1$ particle coming from right

reflection probability $P_R = |B_+|^2$ transmission $P_T = |A_-|^2$

## • BOUND STATES

The wave function $\varphi_n = e^{i\varkappa n}$ can not represent bound state, because it is not normalizable $\sum_n |\varphi_n|^2 = \infty$ for $\varkappa \in \mathbb{R}$. Interestingly the relation $E = \varepsilon_0 - 2b\cos\varkappa = \varepsilon_0 - b(e^{i\varkappa} + e^{-i\varkappa})$ can also be fulfilled with complex $\varkappa$. Requirement of $E \in \mathbb{R}$ allows only two possibilities:

a) $\varkappa = \mp ic$ (assume $c>0$)

$\Rightarrow E = \varepsilon_0 - 2b\cosh c < \varepsilon_0 - 2b$ (*)

Solution to (1) for $n<0$ and for $n>0$

$\varphi_n^L = A_+ e^{cn} + \cancel{A_- e^{-cn}}$ ; $\varphi_n^R = \cancel{B_+ e^{cn}} + B_- e^{-cn}$

not normalizable at $n \to \pm\infty$

+ continuity at $n=0$ $\varphi_0^L = A_+ = \varphi_0^R = B_- = 1$

b) $\varkappa = \mp ic + \pi$ (assume $c>0$)

$\Rightarrow E = \varepsilon_0 + 2b\cosh c > \varepsilon_0 + 2b$ (*)

solution $n<0$ $n>0$

$\varphi_n^L = A_+(-e^{c})^n + \cancel{A_-(-e^{-c})^n}$ ; $\varphi^R = \cancel{B_+(-e^{c})^n} + B_-(-e^{-c})^n$

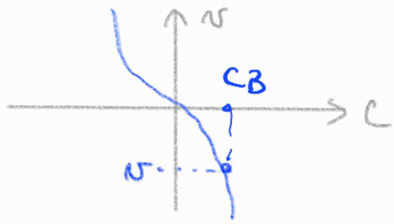
not normalizable at $n \to \pm\infty$

continuity ... $A_+ = A_- = 1$
(normalization found later)

To find the exact value of E we have to find value of c from (2) and (*):

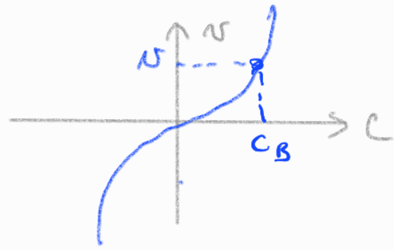
a) $\underbrace{E = \varepsilon_0 - b(e^{c} + e^{-c})}_{(*)} = \underbrace{\varepsilon_0 + v - b(e^{-c} + e^{-c}) = E}_{(2)}$

$\Rightarrow \boxed{v = b(e^{-c} - e^{c}) = -2b\sinh c}$




b) $\underbrace{E = \varepsilon_0 + b(e^{c} + e^{-c})}_{(*)} = \underbrace{\varepsilon_0 + v + b(e^{-c} + e^{-c}) = E}_{(2)}$

$\Rightarrow \boxed{v = b(e^{c} - e^{-c}) = 2b\sinh c}$




**CONCLUSION:** since we need $c>0$ we observe that the case a) applies for $v<0$ and case b) for $v>0$. and we have one state a) below b) above conduction band with $E = \varepsilon_0 \mp 2b\cosh c_B$ ; where $c_B = \mp \sinh^{-1}\frac{v}{2b}$.

**NOTE:** We will return to the chain with deffect when discussing the scattering theory ...