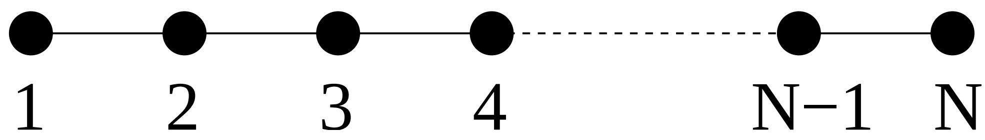
PY4T01 Condensed Matter Theory: Lecture 5

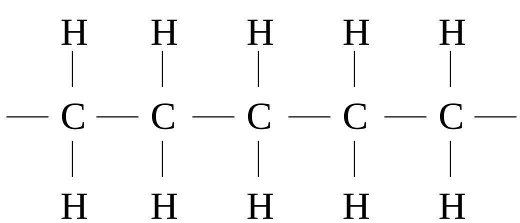
Going from molecules to solids: the H_N linear molecule

Consider the H_N molecule.

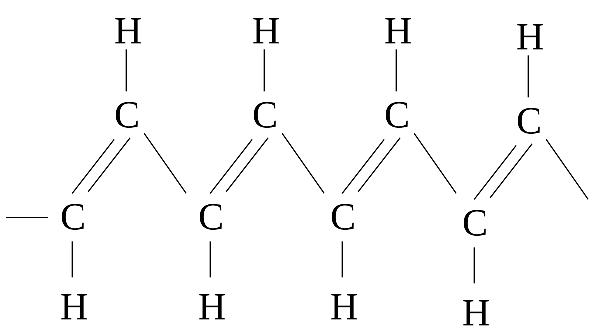


Note that the H_n molecule does not exist in reality since H_2 molecule is very stable. However there are several examples of molecular linear chains:

- Polyethylene: C_2H_6+CH_2+CH_2+.....CH_2=C_nH_{2n+2}



- Polyacetylene: C_2H_4+$(CH)_2$+$(CH)_2$+.....C_nH_{n+2}



We follow the same philosophy of the H_2 molecule:

1. Associate each H atom with an s state: j-th atom $\rightarrow |j\rangle$

2. Expand the molecular wave function $|\psi\rangle$ on such basis

$$|\psi\rangle = \sum_j^N \psi_j |j\rangle$$

3. Find $|\psi\rangle$ and its energy E by solving the Schrödinger equation:

$$H|\psi\rangle = E|\psi\rangle$$

4. Expand the Schrödinger equation on our basis:

$$\sum_j^N \psi_j H|j\rangle = E\sum_i^N \psi_j |j\rangle$$

5. Reduce the Schrödinger equation to a matrix equation (multiply to the left by $\langle i|$)

$$\sum_j^N \psi_j \langle i|H|j\rangle = E\sum_j^N \psi_j \langle i|j\rangle$$

Now we have to decide the values of the matrix elements $\langle i|H|j\rangle$ and the overlaps $\langle i|j\rangle$

We assume:

$$\langle i|j\rangle = \delta_{ij}$$

and

$$\langle i|H|j\rangle = \begin{cases} \epsilon_0 & \text{if} \quad i=j \\ \gamma & \text{if} \quad j = i \pm 1 \\ 0 & \text{elsewhere} \end{cases}$$

This is the <u>tight-binding</u> nearest neighbors approximation

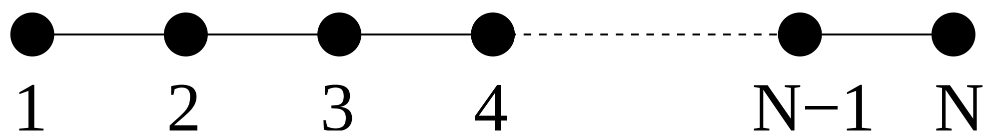
Therefore the secular equation is:

$$\begin{pmatrix} \epsilon_0 & \gamma & 0 & ... & ... \\ \gamma & \epsilon_0 & \gamma & ... & ... \\ 0 & \gamma & \epsilon_0 & ... & ... \\ ... & ... & ... & ... & ... \\ 0 & 0 & 0 & \gamma & \epsilon_0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ ... \\ \psi_n \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ ... \\ \psi_n \end{pmatrix}$$

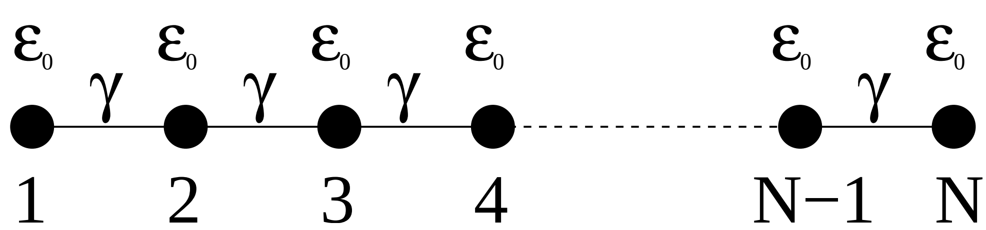
Finite hermitian matrix → diagonalize it → <u>**molecule spectrum**</u>

Graphical way to construct the Hamiltonian matrix

1. Draw the atoms assigning positions



2. Assign on-site energies and hopping integrals



3. Construct the Hamiltonian: element H_{ij}=H^*_{ji} is that between atoms i and j

Now solve the secular equation

$$(\epsilon_0 - E)\psi_1 + \gamma\psi_2 = 0$$

$$\gamma\psi_1 + (\epsilon_0 - E)\psi_2 + \gamma\psi_3 = 0$$

$$\gamma\psi_2 + (\epsilon_0 - E)\psi_3 + \gamma\psi_4 = 0$$

.....

$$\gamma\psi_{N-2} + (\epsilon_0 - E)\psi_{N-1} + \gamma\psi_N = 0$$

$$\gamma\psi_{N-1} + (\epsilon_0 - E)\psi_N = 0$$

Except the first and the last all the equations have the form

$$\gamma\psi_{j-1} + (\epsilon_0 - E)\psi_j + \gamma\psi_{j+1} = 0$$

Let us try the solution

$$\psi_j = \mathrm{e}^{iKj}$$

We have:

$$(\epsilon_0 - E) + \gamma(\mathrm{e}^{iK} + \mathrm{e}^{-iK}) = 0$$

$$E = \epsilon_0 + 2\gamma \cos K$$

If we now consider $K \to -K$ we still have the same solution. Then the most general solution is:

$$\psi_j = A\mathrm{e}^{iKj} + B\mathrm{e}^{-iKj}$$

We fix A and B by using $(\epsilon_0 - E)\psi_1 + \gamma\psi_2 = 0$

$$A\mathrm{e}^{2iK} + B\mathrm{e}^{-2iK} = 2\cos K(A\mathrm{e}^{iK} + B\mathrm{e}^{-iK})$$

This is solved for $A = -B$ and therefore the solution becomes

$$\psi_j = 2iA\sin Kj = C\sin Kj$$

Finally we use the last equation $\gamma\psi_{N-1} + (\epsilon_0 - E)\psi_N = 0$

$$\gamma \sin[(N-1)K] + (\epsilon_0 - E)\sin[NK] = 0$$

After a few algebra this reduces to:

$$\sin[(N+1)K] = 0$$

with solutions

$$K = \frac{m\pi}{N+1} \quad \text{with} \quad m = 1, 2....N$$

Finally we have obtained the spectrum of the H_N molecule

$$E_m = \epsilon_0 + 2\gamma \cos\left(\frac{m\pi}{N+1}\right)$$

and its eigenvalues $|\psi^m\rangle = \sum_j^N \psi_j^m |j\rangle$ where

$$\psi_j^m = \left(\frac{2}{N+1}\right)^{1/2} \sin\left(\frac{m\pi}{N+1} j\right)$$

Now analyze the solutions

$\underline{N = 2}$

$$E_m = \epsilon_0 + 2\gamma \cos\left(\frac{m\pi}{3}\right) \rightarrow \begin{cases} E_1 = \epsilon_0 + \gamma \\ \\ E_2 = \epsilon_0 - \gamma \end{cases}$$

$$\psi_j^m = \left(\frac{2}{3}\right)^{1/2} \sin\left(\frac{m\pi}{3} j\right) \rightarrow \begin{cases} \psi_j^1 = 1/\sqrt{2} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ \\ \psi_j^2 = 1/\sqrt{2} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \end{cases}$$

This corresponds to the bonding ($m = 1$) and antibonding $m = 2$ states of the H_2 molecule.

$\underline{N \to \infty}$

This means that both N and $m \to \infty$ however:

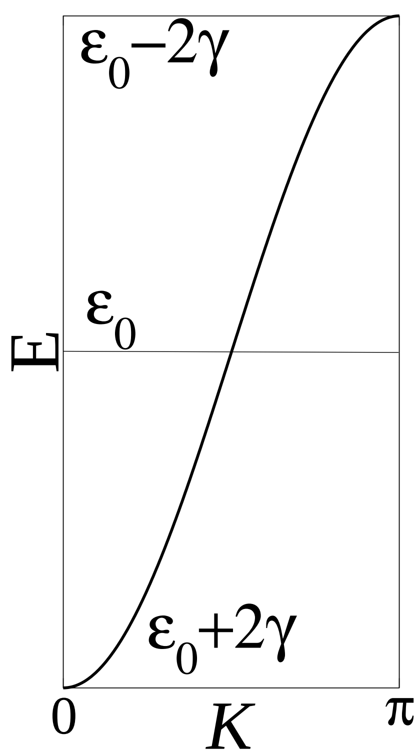
$$K = \frac{m\pi}{N+1} = \pi\frac{m}{N}\frac{1}{1+1/N} \to \pi\frac{m}{N}$$

so

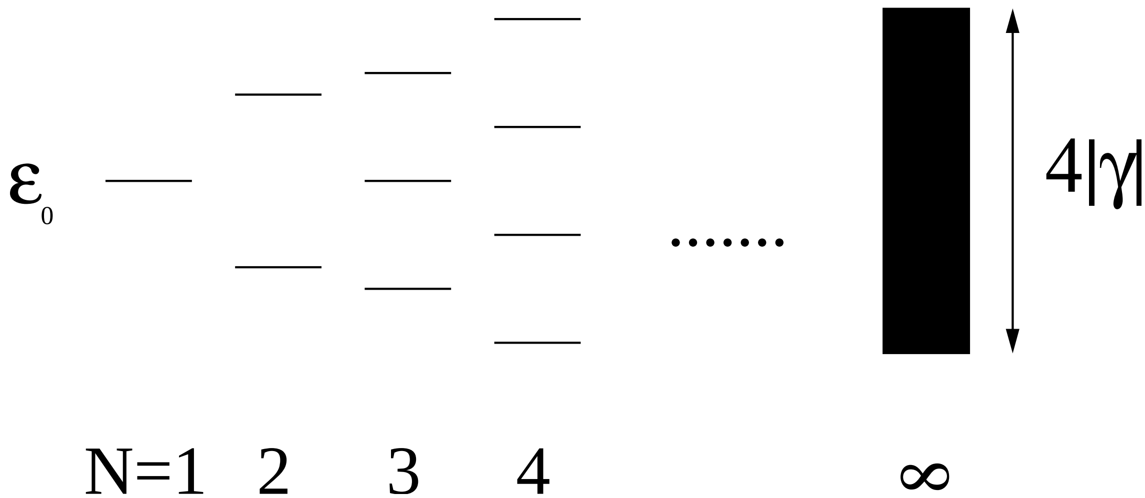
$$E_m \to E_K = \epsilon_0 + 2\gamma\cos K \qquad \text{with} \qquad 0 < K < \pi$$

This is called **energy band** or also **dispersion relation**. In this case:

$$E_{m+1} - E_m \to 0 \qquad \text{and} \qquad \Delta = E_\infty - E_0 = 4|\gamma|$$

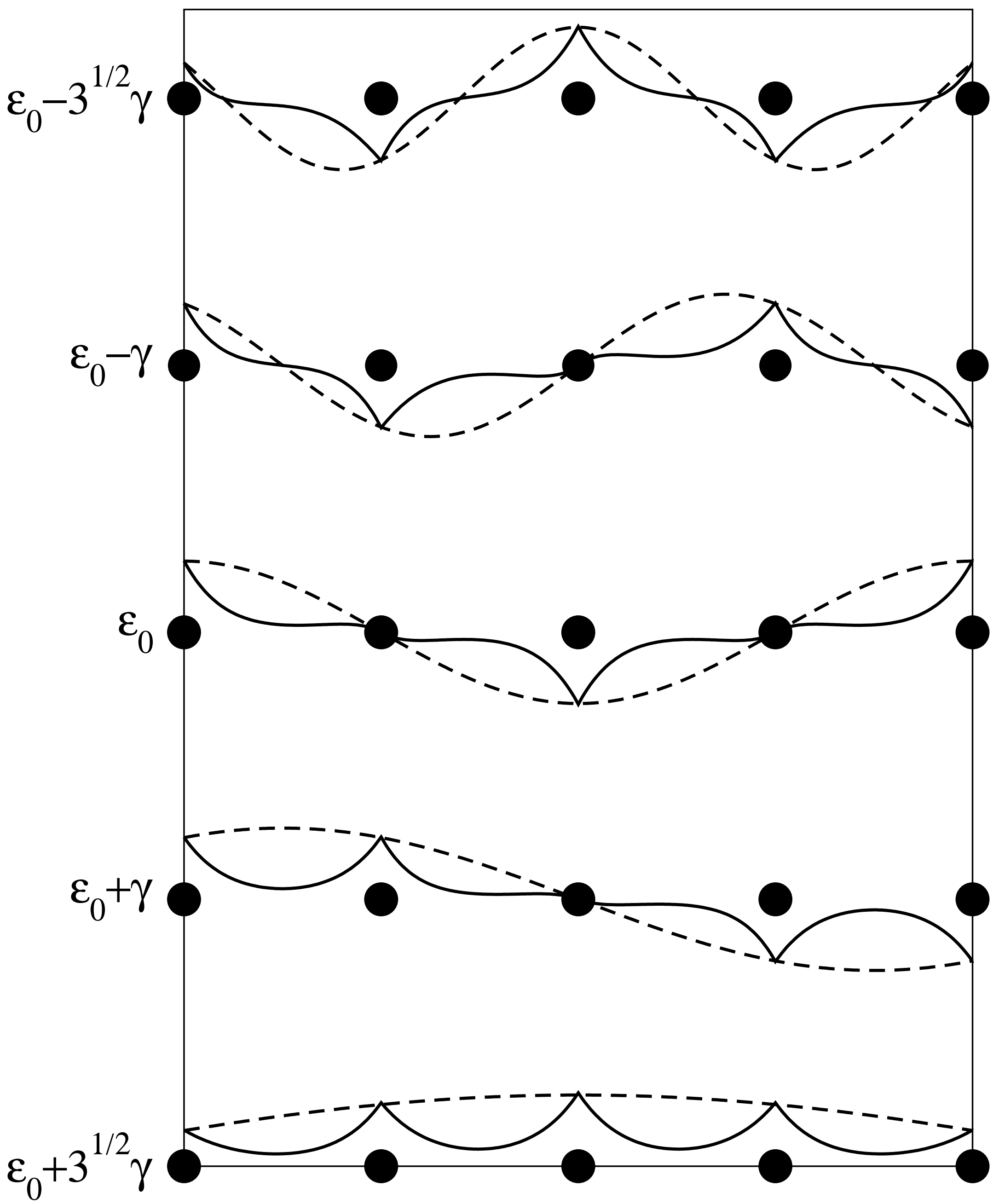


$N \neq 2$ and $N \neq \infty$



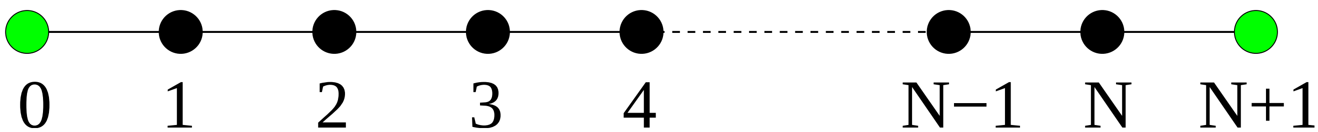
Remember that

$$|\psi_m\rangle = \sum_j \psi_j^m |j\rangle = \sum_j \left(\frac{2}{N+1}\right)^{1/2} \sin\left(\frac{m\pi}{N+1}j\right)|j\rangle$$



Alternative derivation of the dispersion relation

1. Introduce two *imaginary* atoms at the position 0 and $N+1$ and the relevant states $|0\rangle$ and $|N+1\rangle$



2. The benefit is that in our Schrödinger equation now we have:

$$(\epsilon_0 - E)\psi_1 + \gamma\psi_2 = 0 \quad \rightarrow \quad \gamma\psi_0 + (\epsilon_0 - E)\psi_1 + \gamma\psi_2 = 0$$

$$\gamma\psi_{N-1} + (\epsilon_0 - E)\psi_N = 0 \quad \rightarrow \quad \gamma\psi_{N-1} + (\epsilon_0 - E)\psi_N + \gamma\psi_{N+1} = 0$$

with solution

$$\psi_j = A\mathrm{e}^{iKj} + B\mathrm{e}^{-iKj}$$

3. Of course we need to ask:

$$\psi_0 = \psi_{N+1} = 0$$

that gives

$$\psi_0 = 0 \quad \longrightarrow \quad A = -B$$

$$\psi_{N+1} = 0 \quad \longrightarrow \quad \sin[(N+1)K] = 0$$

This derivation reduces the problem to a boundary conditions problem. It is analogous to the problem of free electron in a box.