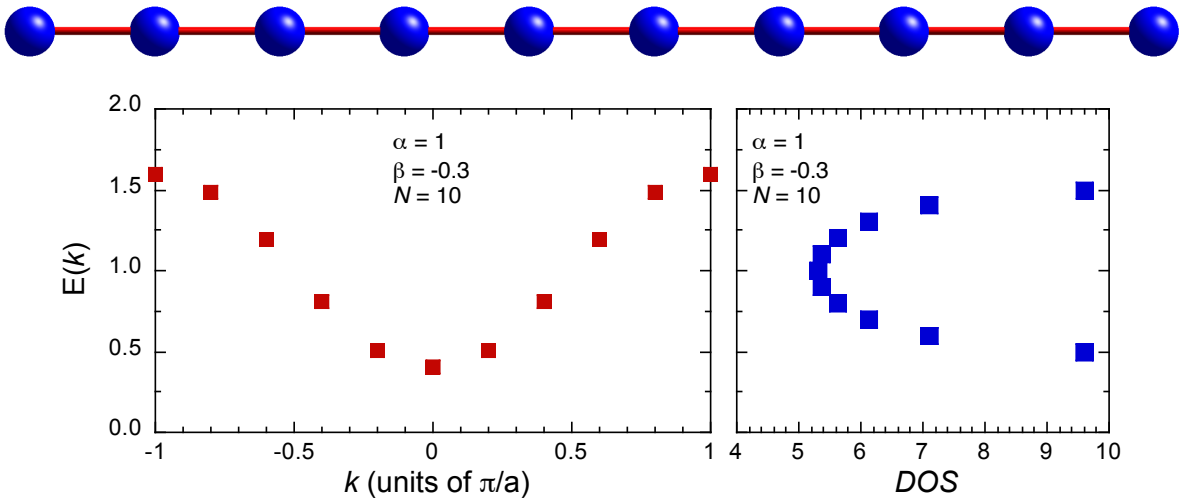
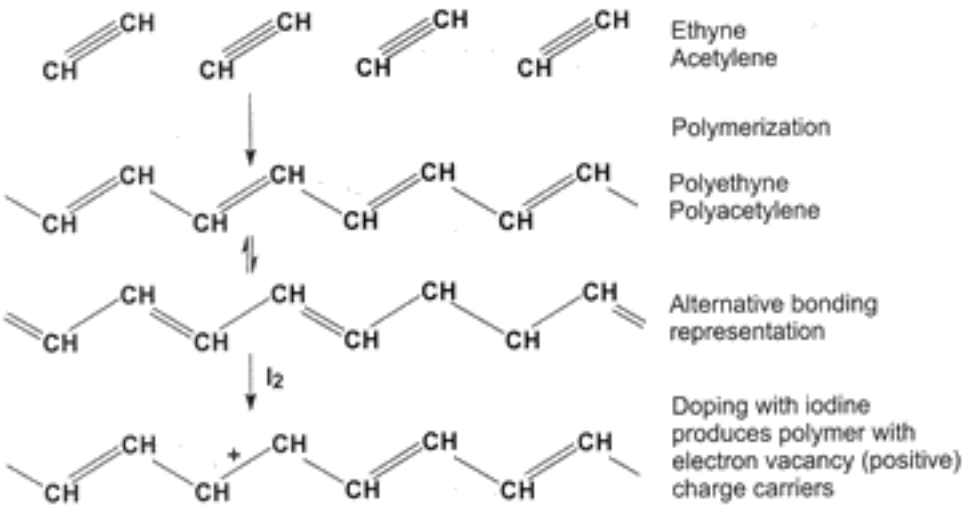
PH575 Spring 2019

Lecture #6:
Linear chain with periodic boundary conditions,
N->∞; *k*-space, Brillouin zones,
(density of states, Bloch functions):
Sutton Ch. 3 pp 44 -> end;
McIntyre Ch 15

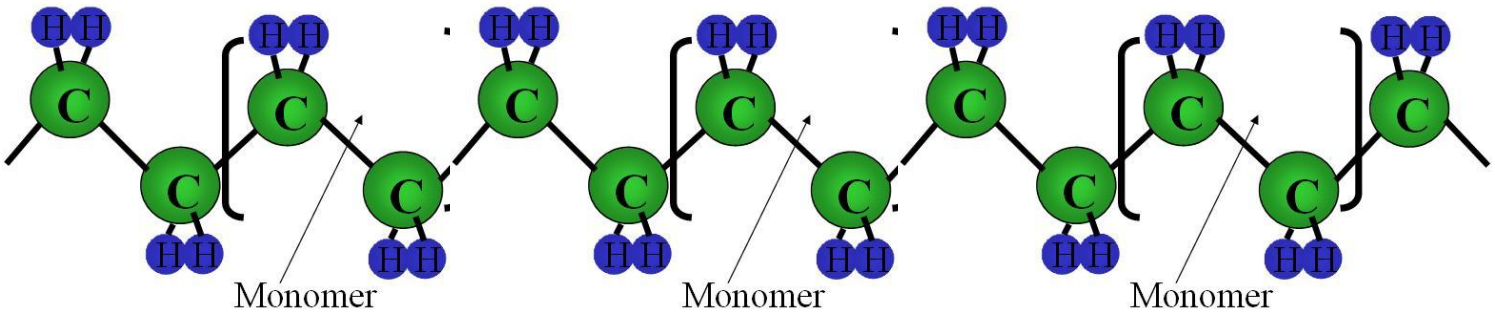


Motivation: Quasi 1-dimensional solids

polyacetylene - highly conducing polymer when doped with I_2

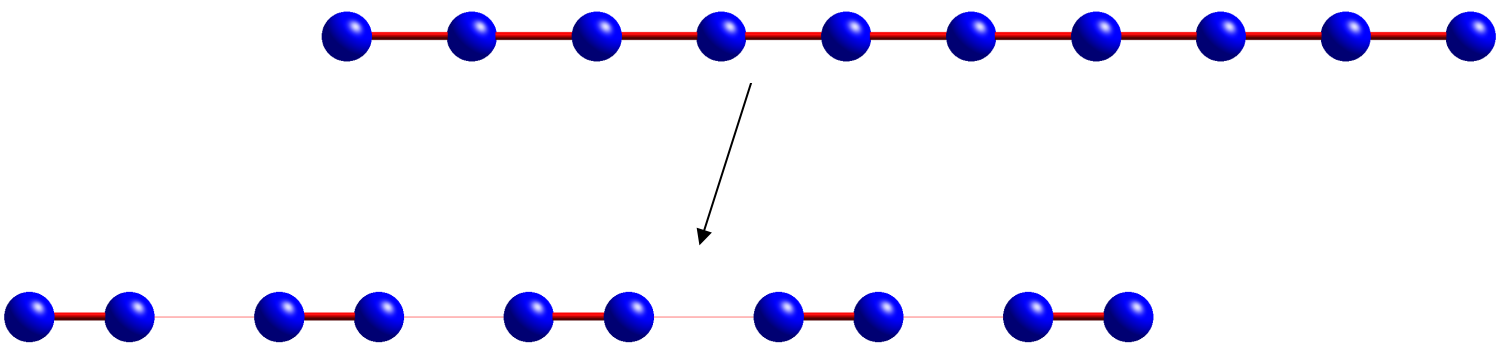


polyethylene - used for hip joints



1-dimensional solids

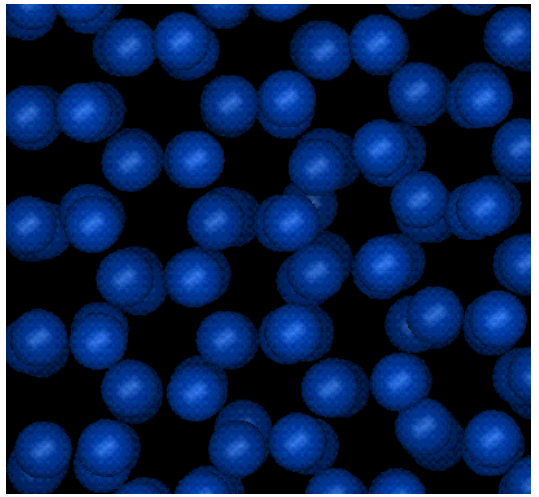
Infinite chain of H atoms (doesn't exist in nature, but good model)



Peierls distortion

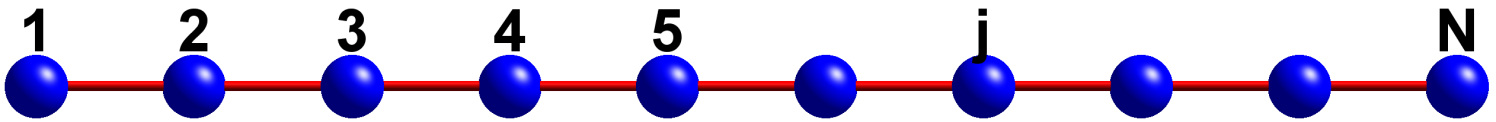
In practice it often leads to systems undergoing a metal-to-insulator transition, as an odd electron count for a metallic 1D chain changes into an even count for a chain of dimers.

3-D H solid is H_2 molecules



voth.hec.utah.edu/ solid_hyd.html

1-dimensional chain of identical atoms



Known atomic orbitals $|j\rangle$,
(*j* labels atom; have suppressed the orbital type – there's only one)

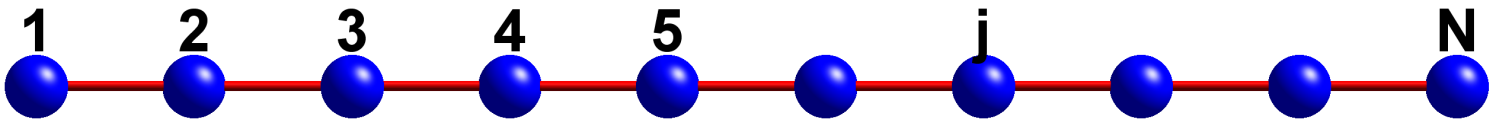
Known Hamiltonian $\hat{H}$

Orthogonal states: $\langle i|j\rangle = \delta_{ij} = \begin{cases} 1 \text{ if } i = j \\ 0 \text{ if } i \neq j \end{cases}$

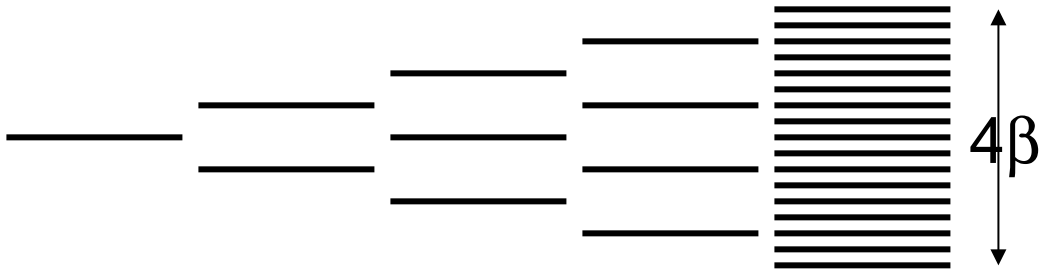
To find: molecular orbitals |Ψ>, and corresponding energies *E*

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad |\Psi\rangle = \sum_{j=1}^{N} c_j |j\rangle$$

1-dimensional chain of identical atoms



How many energy levels?

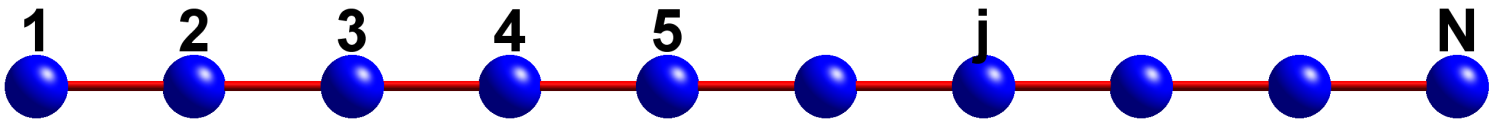


New assumption: nearest neighbor coupling only

$$\langle i|\hat{H}|j\rangle = \begin{cases} \alpha \text{ if } i = j \\ \beta \text{ if } i = j \pm 1 \\ 0 \text{ otherwise} \end{cases}$$

$$\hat{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 \\ \beta & \alpha & \beta & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

1-dimensional chain of identical atoms



$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad |\Psi\rangle = \sum_{j=1}^{N} c_j |j\rangle$$

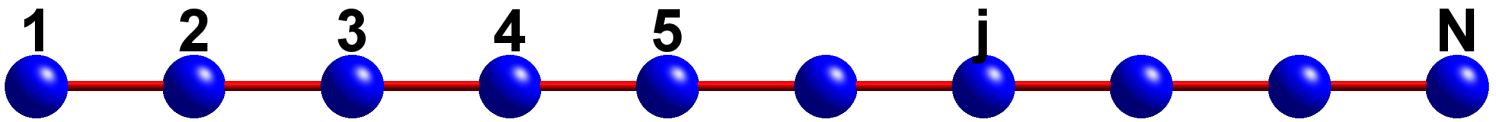
$$\sum_{j=1}^{N} c_j \hat{H}|j\rangle = E\sum_{j=1}^{N} c_j |j\rangle \xrightarrow{\text{project onto } \langle p|}$$

$$\sum_{j=1}^{N} c_j \langle p|\hat{H}|j\rangle = E\sum_{j=1}^{N} c_j \langle p|j\rangle$$

$$= Ec_p$$

This can be written in matrix form, just like the 2-atom case!

1-dimensional chain of identical atoms

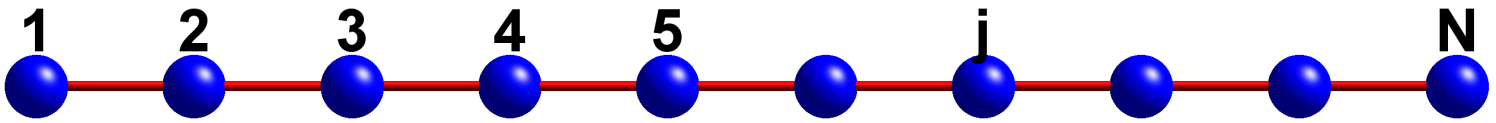


$$\sum_{j=1}^{N} c_j \langle p | \hat{H} | j \rangle = E c_p$$

$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & \beta & \alpha - E & \beta \\ 0 & 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ \cdots \\ c_j \\ \cdots \\ c_N \end{pmatrix} = 0$$

Sutton Eq. 3.5 -> solve by setting determinant = 0 ☹

1-dimensional chain of identical atoms

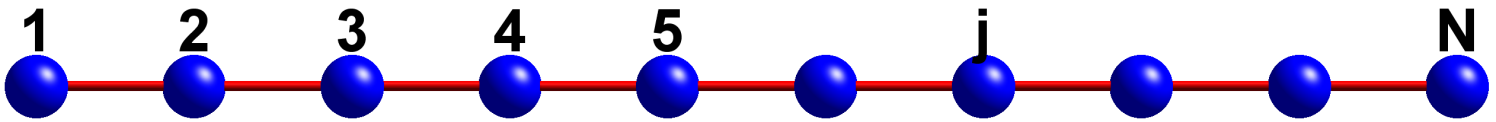


$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & \beta & \alpha - E & \beta \\ 0 & 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ \cdots \\ c_j \\ \cdots \\ c_N \end{pmatrix} = 0$$

N coupled equations (except for two ends):

$$c_{j-1} - \frac{(E-\alpha)}{\beta} c_j + c_{j+1} = 0$$

1-dimensional chain of identical atoms



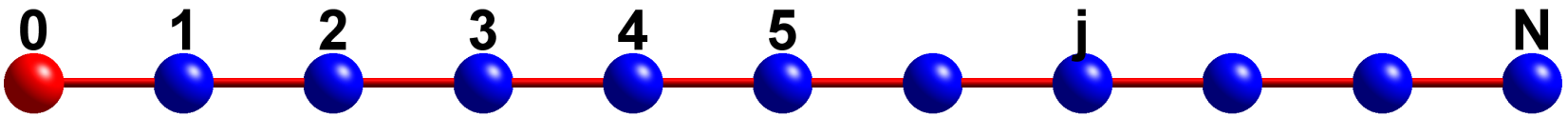
Can we make the problem simpler if N becomes large?

Yes!

If we don't care about the ends (what's a few atoms in 10^{23}?) then we can invoke periodic boundary conditions.

We make an imaginary extra atom "0", and make it identical to "N"

1-dimensional chain of identical atoms

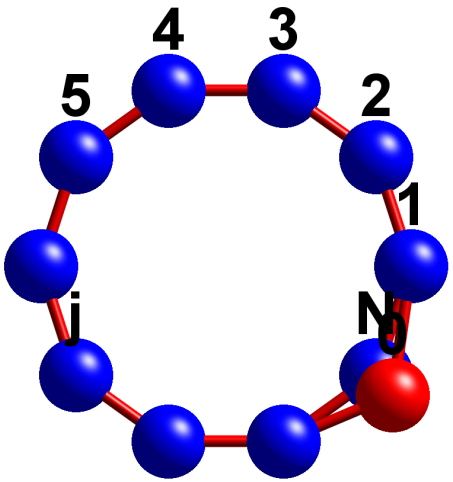


Strategy: Guess form of the *c* coefficients and see if that works

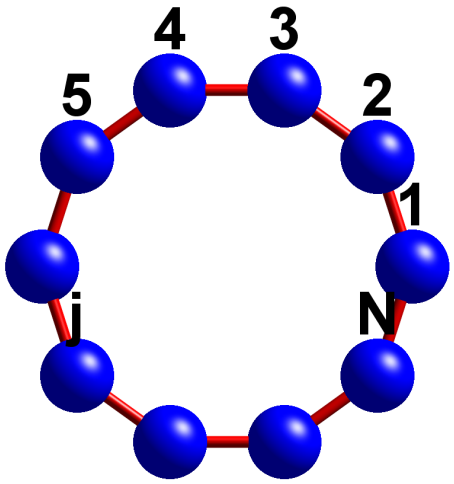
Trick: Imaginary 0^{th} atom coincides with the N^{th} atom

Periodic boundary conditions Demand $c_0 = c_N$

(The chain remains linear, but it helps to imagine a circle)



1-dimensional chain of identical atoms



* Remember the molecule is LINEAR! This ring is just a memory device

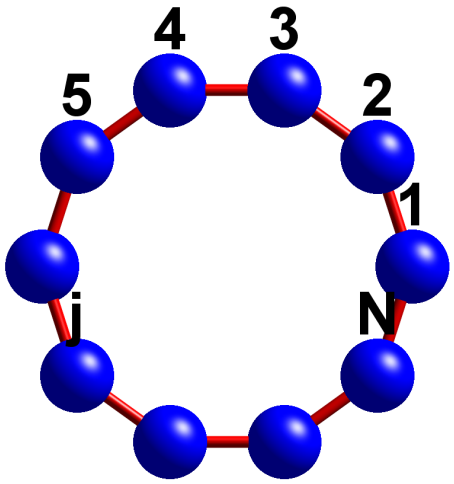
Guess: $c_j = Ae^{ij\theta}$

Why is this reasonable?
What does it mean?

c_j is contribution of each atomic orbital – should be **same size** for each *i*, because of symmetry.

Only way to do this is for each each orbital to have a different phase (which does not change its size), but which can give it an imaginary part!

1-dimensional chain of identical atoms



$$c_j = Ae^{ij\theta}$$

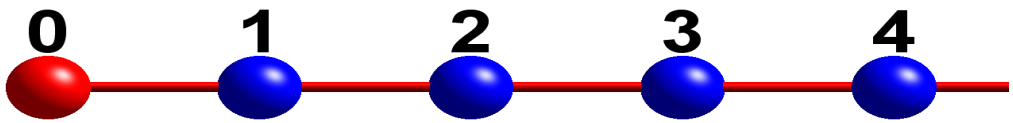
$$c_0 = c_N \Rightarrow A = Ae^{iN\theta} \Rightarrow 1 = e^{iN\theta}$$

$$\Rightarrow \theta = \frac{2m\pi}{N} \text{ where } m = 0,1,2....N-1$$

why?

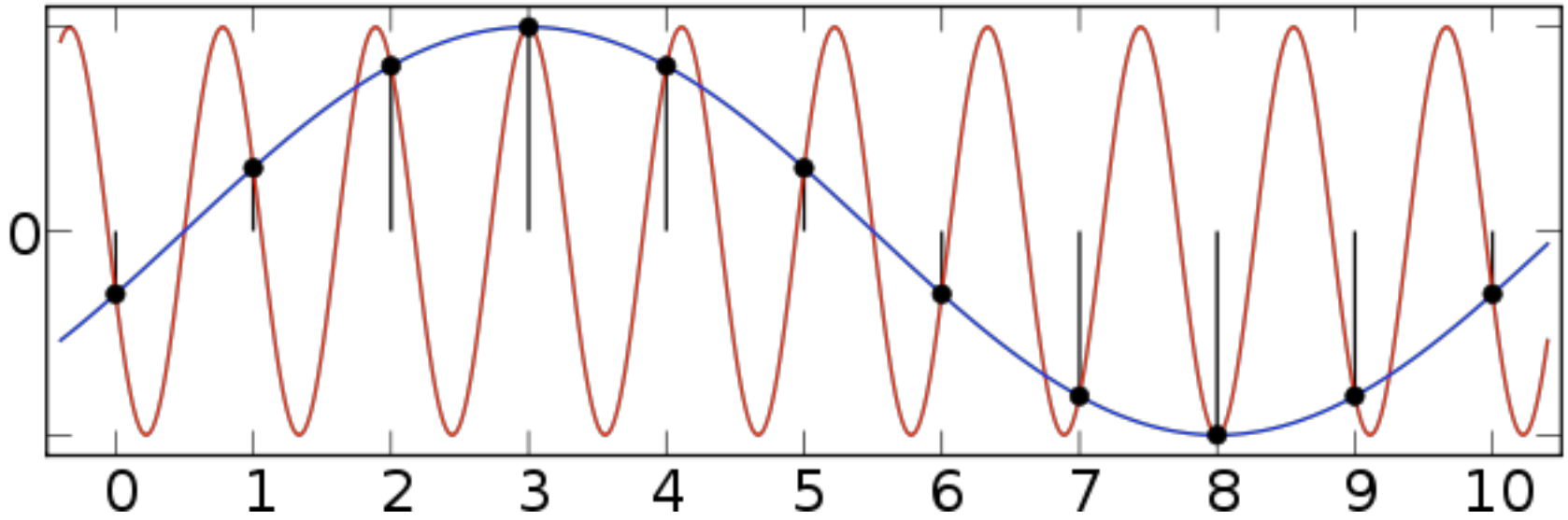
$$c_j^{(m)} = Ae^{ij\left(\frac{2m\pi}{N}\right)}$$

Note TWO counting indices:
j labels atoms,
m labels..what?



#cycles	c_0	c_1	c_2	c_3	c_4
$m = 0$	e^{i0}	e^{i0} 1	e^{i0} 1	e^{i0} 1	e^{i0} 1
$m = 1$	e^{i0}	$e^{i\pi/2}$ i	$e^{i2\pi/2}$ -1	$e^{i3\pi/2}$ $-i$	$e^{i2\pi}=e^{i0}$ 1
$m = 2$	e^{i0}	$e^{i\pi}$ -1	$e^{i2\pi}$ 1	$e^{i3\pi}$ -1	$e^{i4\pi}=e^{i0}$ 1
$m = 3$	e^{i0}	$e^{i3\pi/2}$ $-i$	$e^{i6\pi/2}$ -1	$e^{i9\pi/2}$ i	$e^{i6\pi}=e^{i0}$ 1
$m = 4$	e^{i0}	$e^{i2\pi}$ 1	$e^{i4\pi}$ 1	$e^{i6\pi}$ 1	$e^{i8\pi}=e^{i0}$ 1

aliasing



1-dimensional chain of identical atoms

Contribution to m^{th} molecular wave function of j^{th} atomic orbital

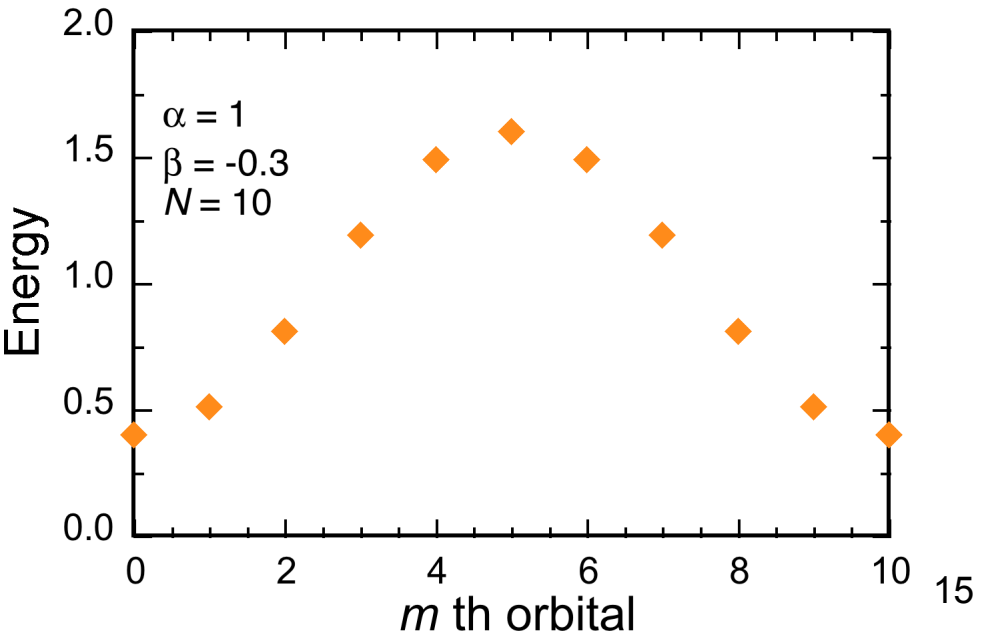
$$c_j^{(m)} = Ae^{ij\left(\frac{2m\pi}{N}\right)}$$

Plug back into:

$$c_{j-1}^{(m)} - \frac{\left(E^{(m)} - \alpha\right)}{\beta} c_j^{(m)} + c_{j+1}^{(m)} = 0$$

$$E^{(m)} = \alpha + 2\beta\cos\left(\frac{2m\pi}{N}\right)$$

Dispersion relation

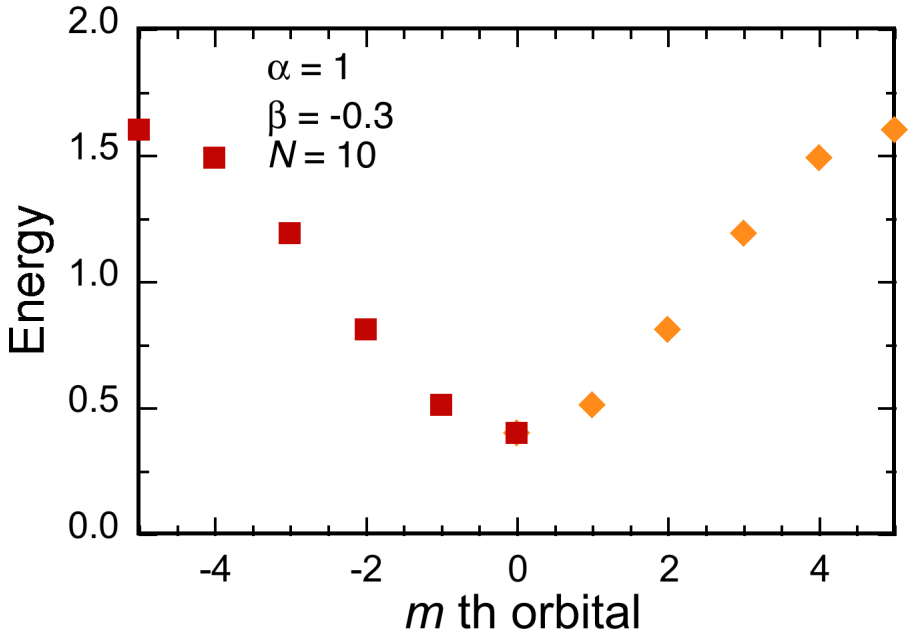


1-dimensional chain of identical atoms

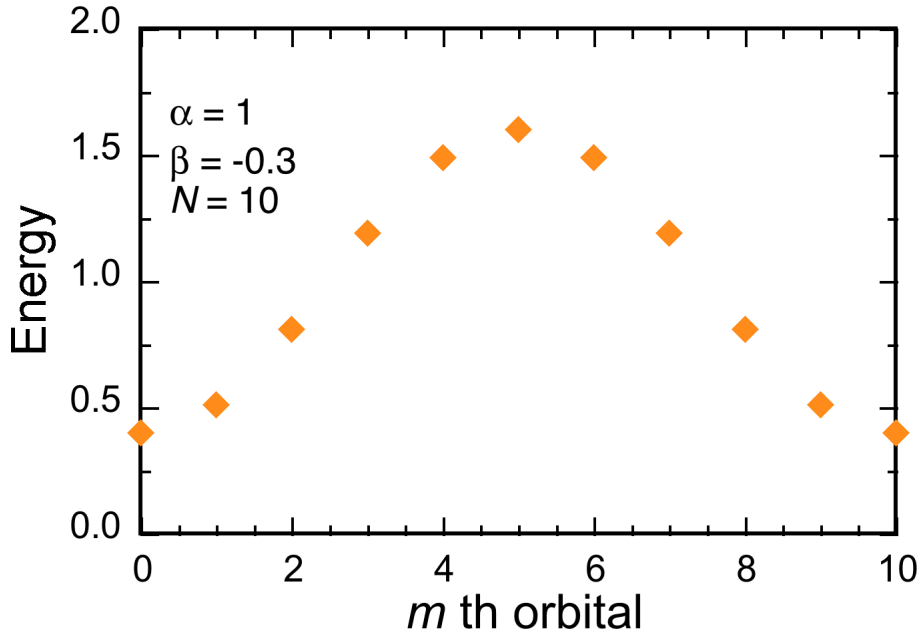
$$E^{(m)} = \alpha + 2\beta\cos\left(\frac{2m\pi}{N}\right)$$

Unique information can be presented in either of 2 forms. The left hand one is conventional.

m = 0, ±1, ±2 …. ±N/2



m = 0, 1, 2 …. N-1



1-dimensional chain of identical atoms

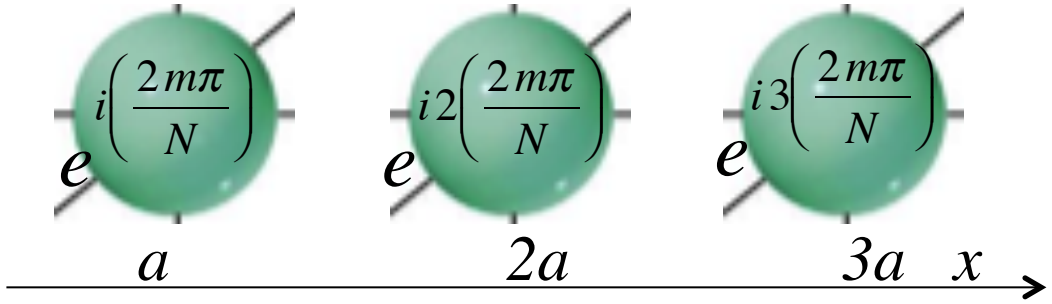
Normalize MO to find *A*: $c_j^{(m)} = Ae^{ij\left(\frac{2m\pi}{N}\right)}$

Normalization: $\left\langle \Psi^{(m)} \middle| \Psi^{(m)} \right\rangle = 1$

$$c_j^{(m)} = \frac{1}{\sqrt{N}} e^{ij\left(\frac{2m\pi}{N}\right)}$$

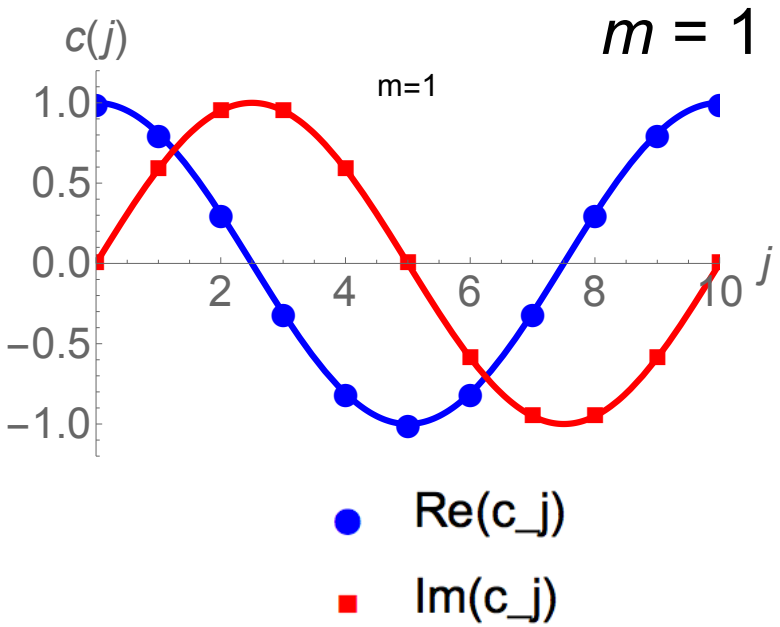
MO: $$\left|\Psi^{(m)}\right\rangle = \frac{1}{\sqrt{N}}\left(e^{i\left(\frac{2m\pi}{N}\right)}\left|1\right\rangle + e^{i2\left(\frac{2m\pi}{N}\right)}\left|2\right\rangle + \ldots + e^{i\left(\frac{2m\pi}{1}\right)}\left|N\right\rangle \right)$$

$\Psi^{(m)}(x)$

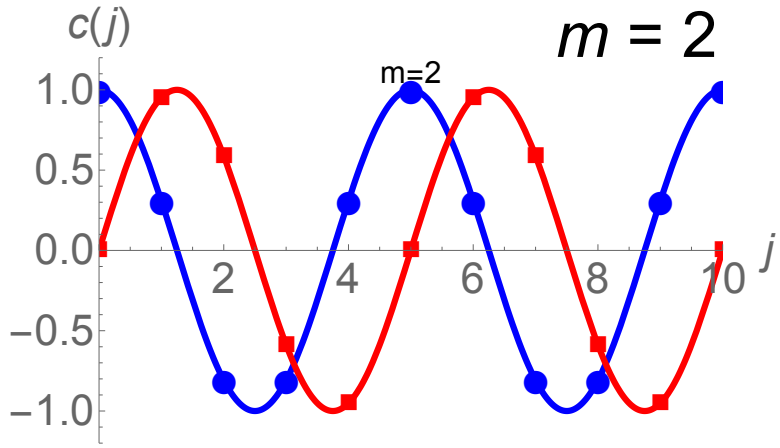


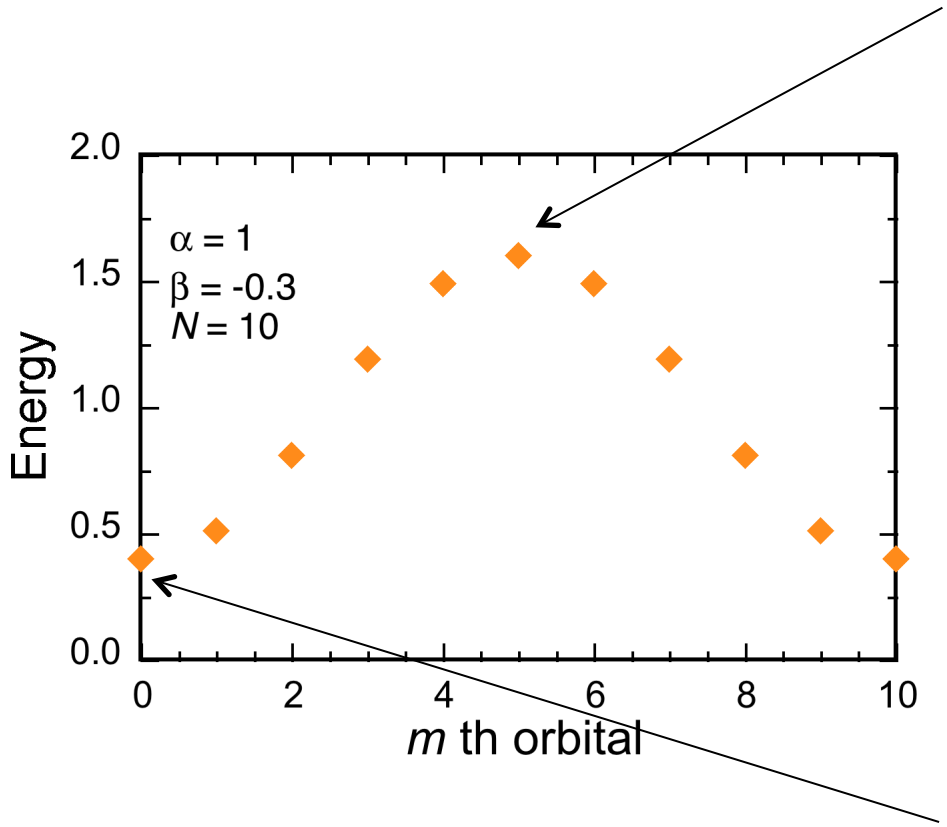
1-dimensional chain of identical atoms

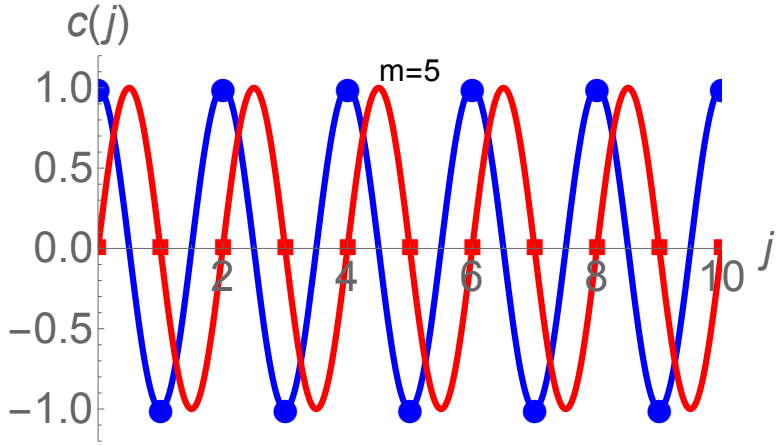
$$c_j^{(m)} = \frac{1}{\sqrt{N}} e^{ij\left(\frac{2m\pi}{N}\right)}$$



Vertical axis: Re and Im parts of $c_j^{(m)}$
Horizontal axis: distance
Each number represents an atom.



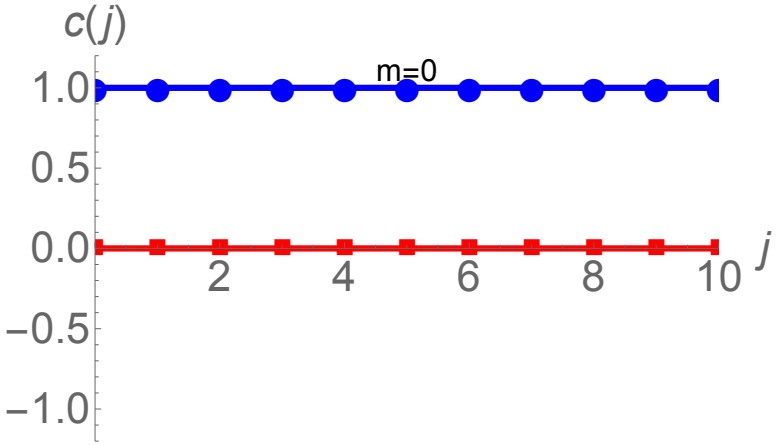




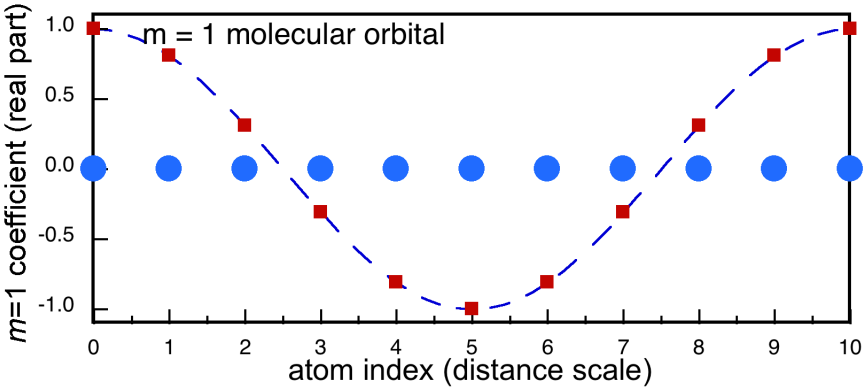
Re(c_j)

Im(c_j)

$m = 0, 10$



k-space: a different label for molecular orbitals



$$k_1 = \frac{2\pi}{\lambda_1} = \frac{1}{N}\frac{2\pi}{a}$$

$$E^{(m)} = \alpha + 2\beta\cos\left(\frac{2m\pi}{N}\right)$$

$$\downarrow$$

$$E(k) = \alpha + 2\beta\cos(ka)$$

a is lattice spacing;
N is number of atoms
Na is length of solid

$$m = \#\ cycles = \frac{Na}{\lambda_m}$$

$$k_m = \frac{2\pi}{\lambda_m} = \frac{m}{N}\frac{2\pi}{a}$$

k_m is an alternative label. Usually we leave off the subscript *m*.

k-space: info in the first Brillouin zone

All unique information about the MOs is contained in the first "**Brillouin zone**".

It has width (in m-space) $\Delta m=N$
It has width (in k-space) $\Delta k=2\pi/a$

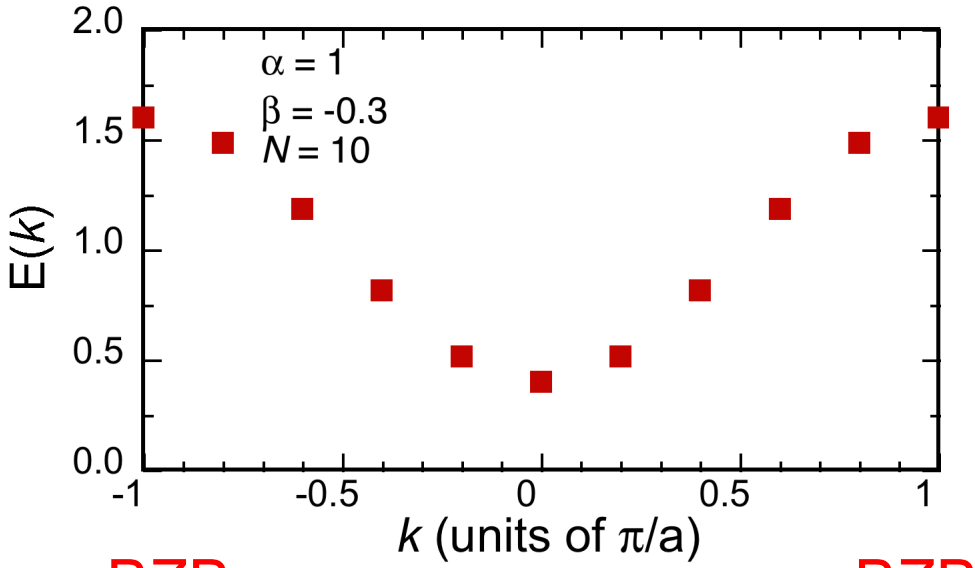
Conventionally, we center it on $k=0$, and then the "edges" are at $k_{BZB} = \pm\pi/a$

Léon Nicolas Brillouin (1889-1969)
http://home.att.net/~numericana/fame/brillouin.jpg

k-space: a different label for molecular orbitals

$$E(k) = \alpha + 2\beta\cos(ka)$$

Instead of labeling MOs with a number *m,* we designate them by the wavelength of the variation of the charge distribution.



BZB BZB

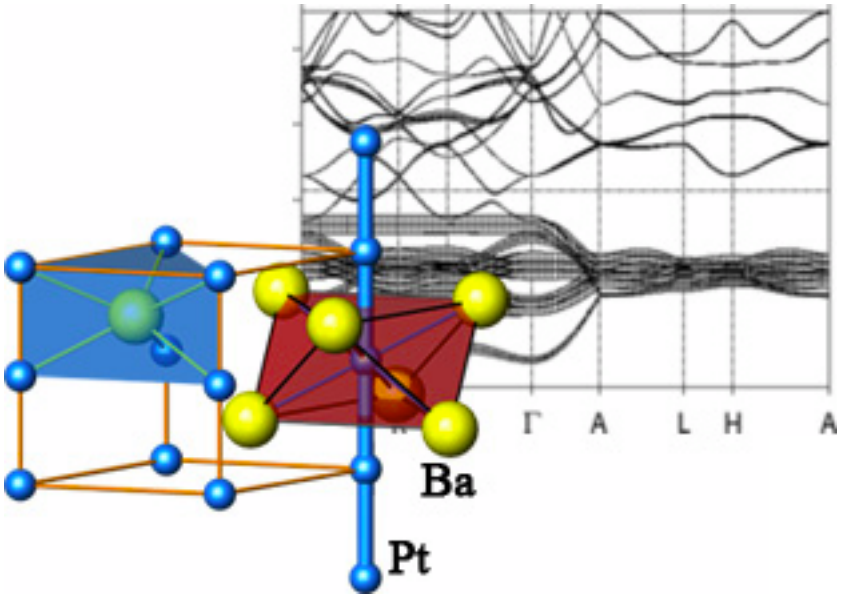
k: dimensions of inverse length

k is a discrete index if there are few atoms/orbitals => E_k

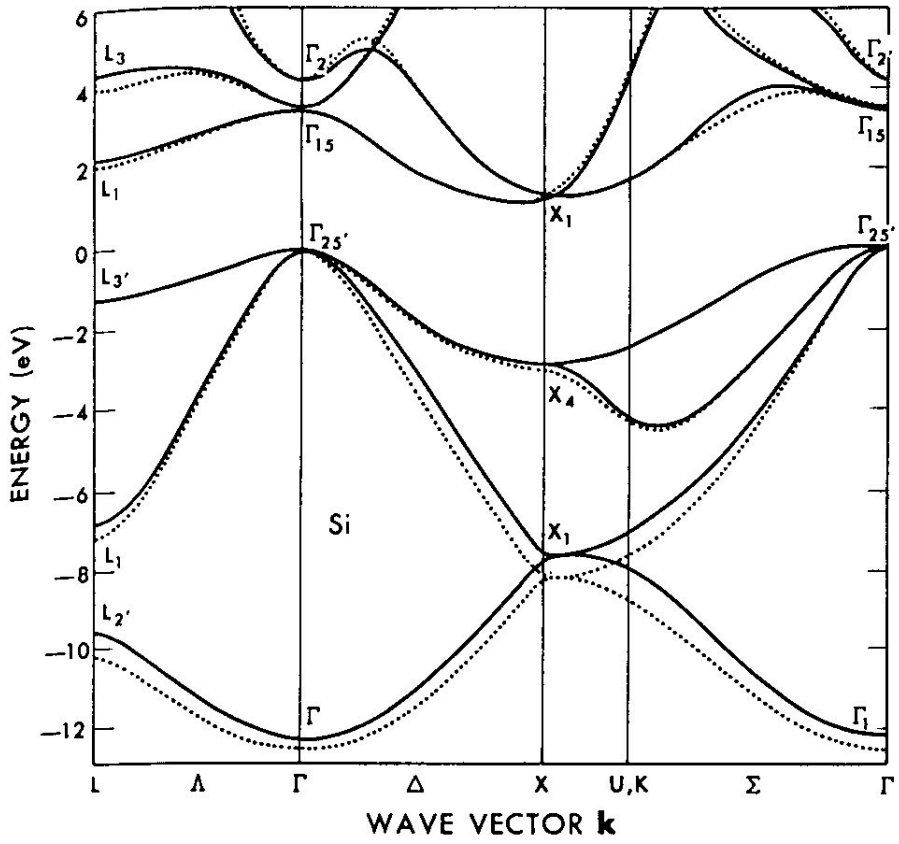
k is a quasi-continuous index if *N* is large => *E*(*k*)

The set of values of *k* is called *k*-space or "reciprocal space"

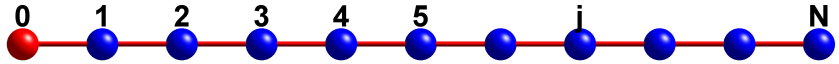
If the "real space" lattice spacing *a* is large (small) then the "reciprocal space" spacing between allowed *k* values is small (large).

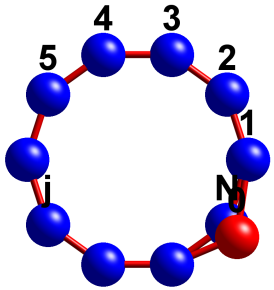


We're almost there …
Just add more dimensions and more orbitals



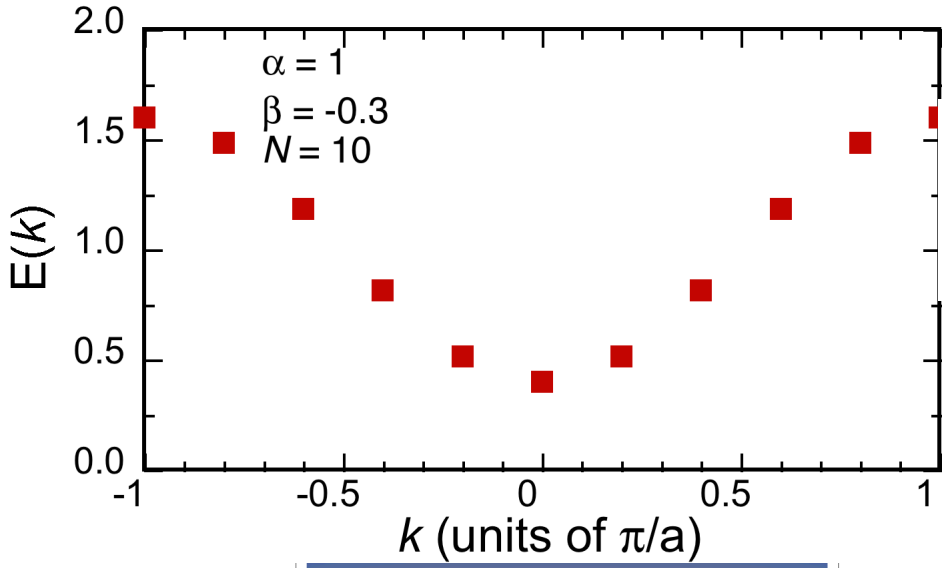
Summary: 1-D Chain, n-n, PBC

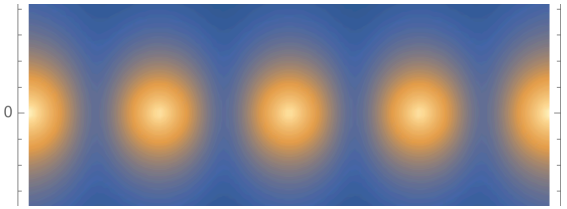




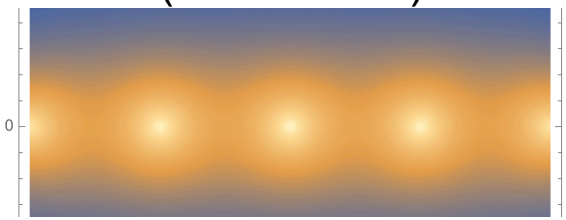
MO $\left|\Psi_m\right\rangle = \sum_{j=1}^{N} \frac{1}{\sqrt{N}} e^{ij\frac{2\pi m}{N}} \left|j\right\rangle$ $\left|\Psi_k\right\rangle = \sum_{j=1}^{N} \frac{1}{\sqrt{N}} e^{ijka} \left|j\right\rangle$

$E^{(m)} = \alpha + 2\beta\cos\left(\frac{2m\pi}{N}\right)$ $E(k) = \alpha + 2\beta\cos(ka)$





BZB



BZB

Bloch's theorem in 1-d

We needed a MO that would give periodically varying probability. Bloch's theorem, for a 1-d system of periodicity (lattice spacing) *a*

$$\Psi^{(k)}(x) = e^{ikx}u(x) \quad \text{(u(x) periodic in a)}$$

$$\left|\Psi^{(k)}(x)\right|^2 = \left|\Psi^{(k)}(x+a)\right|^2$$

Felix Bloch (1905 – 1983)
http://en.wikipedia.org/wiki/Felix_Bloch

Bloch waves