Lecture #5&6
Linear chain with periodic boundary conditions, $N \to \infty$; $k$-space, Brillouin zones, density of states, (Bloch functions):
Sutton Ch. 3 pp 44 -> end;
McIntyre Ch 15
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 H₂ molecules

voth.hec.utah.edu/solid_hyd.html
Quasi 1-dimensional solids

Polyacetylene - highly conducting polymer when doped with $I_2$

Polyethylene - used for hip joints
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 $|\Psi\rangle$, and corresponding energies $E$

$\hat{H} |\Psi\rangle = E |\Psi\rangle$  \quad $|\Psi\rangle = \sum_{j=1}^{N} c_{j} |j\rangle$
1-dimensional chain of identical atoms

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

New assumption: nearest neighbor coupling only

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

How many energy levels? a ___________ ___________ ___________ ___________ 

\[ N=2 \quad N=3 \quad N=4 \quad N=\infty \]

How many energy levels?
1-dimensional chain of identical atoms

\[ \hat{H} |\Psi\rangle = E |\Psi\rangle \quad |\Psi\rangle = \sum_{j=1}^{N} c_j |j\rangle \]

\[ \sum_{j=1}^{N} c_j \hat{H} |j\rangle = E \sum_{j=1}^{N} c_j |j\rangle \]

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

\[ = Ec_p \]

This can be written in matrix form, just like the 2-atom case!
1-dimensional chain of identical atoms

\[ \sum_{j=1}^{N} c_j \left< p \left| \hat{H} \right| j \right> = E c_p \]

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

\( N \) coupled equations:

\[ c_{j-1} - \left( \frac{E - \alpha}{\beta} \right) c_j + c_{j+1} = 0 \]

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 ends):

\[c_{j-1} - \left(\frac{E - \alpha}{\beta}\right)c_j + c_{j+1} = 0\]
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
Demand $c_0 = c_N$

**Periodic boundary conditions**: useful when details of the surface are unimportant
ring is large enough
1-dimensional ring of identical atoms

Guess: \( c_j = Ae^{ij\theta} \)

Why is this reasonable?
What does it mean?

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

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

Note TWO counting indices:
\( j \) labels atoms,
\( m \) labels...what?
aliasing
1-dimensional ring of identical atoms

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

Plug back into:

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

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

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

Dispersion relation
1-dimensional ring 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.

\[ m = 0, \pm 1, \pm 2 \ldots \pm N/2 \]

\[ m = 0, 1, 2 \ldots N-1 \]
1-dimensional ring of identical atoms

Normalize MO to find $A$:

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

Normalization:

$$\langle \Psi^{(m)} | \Psi^{(m)} \rangle = 1$$

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

MO:

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

$$\Psi^{(m)}(x)$$
1-dimensional ring of identical atoms

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

$$|\Psi^{(m)}(x)|^2 = |\Psi^{(m)}(x + a)|^2$$
1-dimensional ring of identical atoms

\[ c_j^{(m)} = \frac{1}{\sqrt{N}} e^{i j \left(\frac{2m\pi}{N}\right)} \]

Vertical axis: Re and Im parts of \( c_j^{(m)} \)
Horizontal axis: distance
Each number represents an atom.
\[ m = 5 \]

\[ m = 0, 10 \]

\[ \alpha = 1 \]
\[ \beta = -0.3 \]
\[ N = 10 \]
**k-space: a different label for molecular orbitals**

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

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

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

$m\lambda_m = Na$

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

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

$a$ is lattice spacing; what is $\lambda_m$ (the wavelength of electron density variation?)
The \( k \) corresponding to the smallest wavelength is called the "Brillouin zone boundary." It marks the edge of the zone of \( k \) values that give unique information.

\[
k_{BZB} = \frac{2\pi}{\lambda_5} = \frac{N}{2} \frac{2\pi}{N a} = \frac{\pi}{a}
\]
**k-space: a different label for molecular orbitals**

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

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

\( k \): dimensions of inverse length

- \( k \) is a discrete index if there are few atoms/orbitals \( \Rightarrow E_k \)
- \( k \) is a quasi-continuous index if \( N \) is large \( \Rightarrow E(k) \)

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

\[ |\Psi_m\rangle = \sum_{j=1}^{N} \frac{1}{\sqrt{N}} e^{ij \frac{2\pi m}{N}} |j\rangle \quad |\Psi_k\rangle = \sum_{j=1}^{N} \frac{1}{\sqrt{N}} e^{ijka} |j\rangle \]

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