Lectures 10,11
Electrons in Crystal

Physicists may say "Bragg diffraction."
Chemists may say "Chemical bonding."
Electrons could not care less.

Bloch's Theorem (review)

Chapter 8, A&M; Should be viewed as describing wave function of any particles, not only electrons.

Form 1

$$\psi_{n\mathbf{k}}(\mathbf{x}) = \exp(i\mathbf{k}\cdot\mathbf{x})\, u_{n\mathbf{k}}(\mathbf{x}),$$

$$u_{n\mathbf{k}}(\mathbf{x}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{x})$$

n includes all other quantum #'s
(spin, polarization, orbital …)

Form 2

$$\psi_{n\mathbf{k}}(\mathbf{x}+\mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R})\, \psi_{n\mathbf{k}}(\mathbf{x})$$

Dynamical Origin of Bloch's Theorem

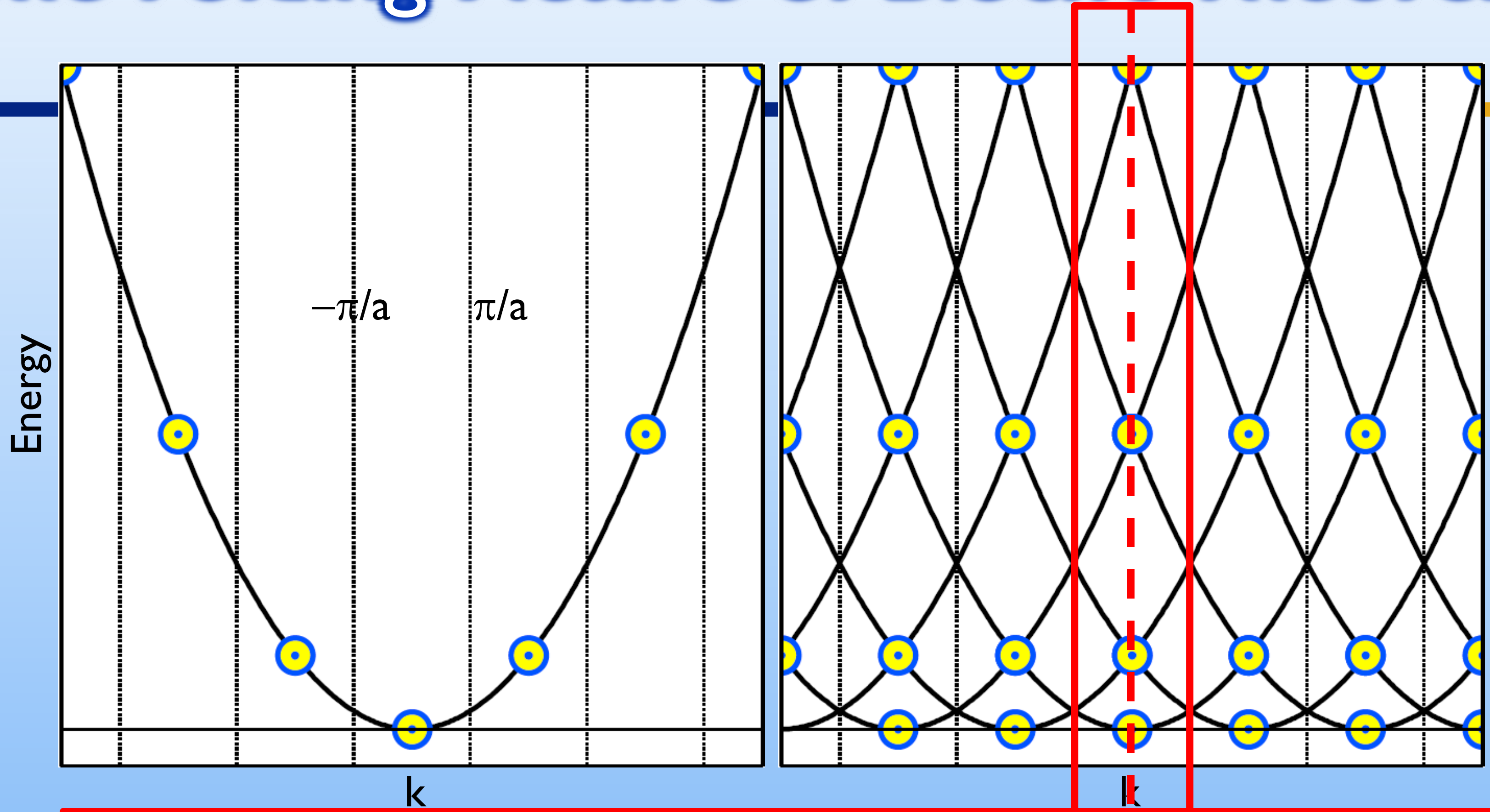
- Hamiltonian $H = T + V$
- In the plane wave basis,

  $$H = \Sigma_{k,K} |k\rangle\langle k|H|k+K\rangle\langle k+K|$$

  As T is already diagonal, it only needs to be seen that $V = \Sigma_{k,k'} |k\rangle\langle k|V|k'\rangle\langle k'| = \Sigma_{k,K} |k\rangle\langle k|V|k+K\rangle\langle k+K|$.

  The last step is the most important (K = R.L. vector), following from the translation symmetry of the crystal.
- Thus, an eigenstate $= \Sigma_{k,K}\, C(K)|k+K\rangle$

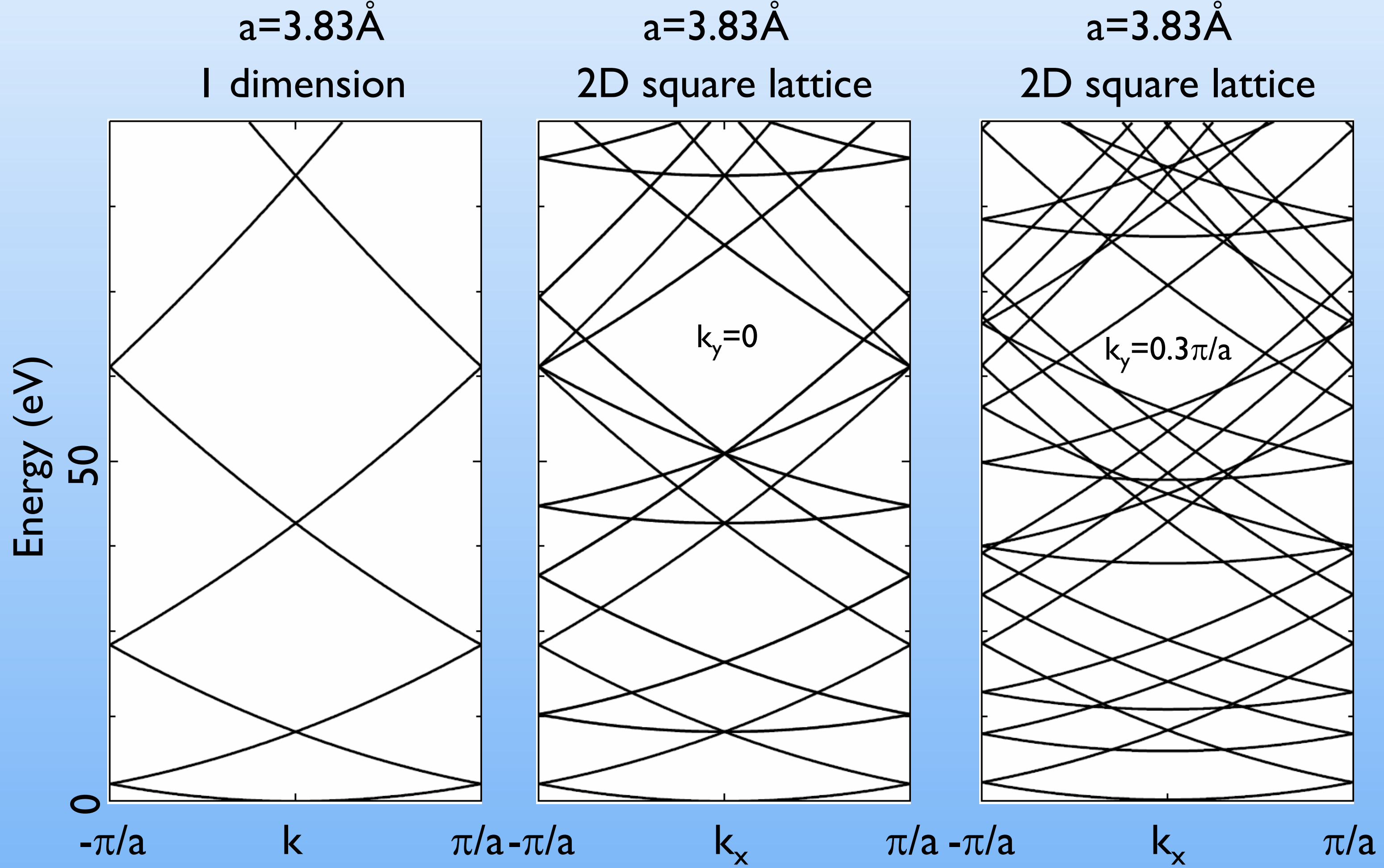
Zone Folding Picture of Bloch's Theorem



Procedure to solve for <u>any</u> crystal potential (not only for weak potential)

1. Start from plane wave
2. Fold the free electron band to the first Brillouin zone
3. Solve the block matrix of H for states along a vertical line

Zone-Folding and dimensionality



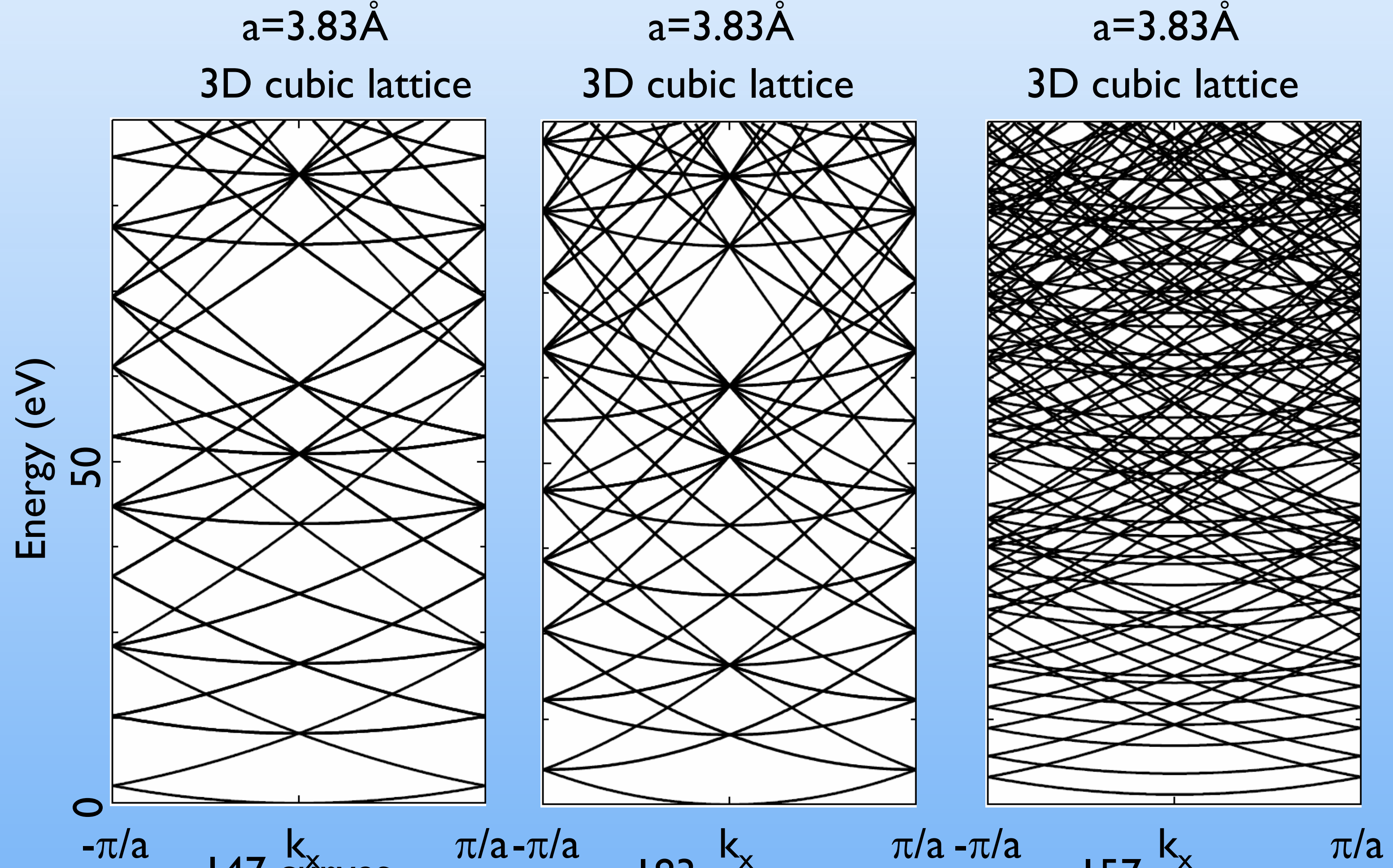
6 curves

37 curves

36 curves

Zone-Folding and dimensionality

Curves ~ A^D, for a given energy range (0 – 100 eV here; with A = 5-6)



147 curves
$k_y=k_z=0$

183 curves
$k_x=k_y$, $k_z=0$

157 curves
$k_y=0.7\pi/a$, $k_z=0.3\pi/a$

Equation of Motion

∞ x ∞ matrix !

$$\begin{bmatrix} \ddots & & \vdots & \vdots & \vdots & \iddots \\ V(1) & \lambda_{k-G}-E & V(1)^* & V(2)^* & V(3)^* & \cdots \\ V(2) & V(1) & \lambda_k-E & V(1)^* & V(2)^* & \cdots \\ \cdots & V(2) & V(1) & \lambda_{k+G}-E & V(1)^* & \cdots \\ \iddots & \vdots & \vdots & \vdots & & \ddots \end{bmatrix} \begin{bmatrix} \vdots \\ c(k-G) \\ c(k) \\ c(k+G) \\ \vdots \end{bmatrix} = 0$$

Toy Problem (Kronig-Penney)

Note: G is reciprocal lattice vector here.

$$V(x) = Aa \sum_{n=1}^{N} \delta(x - na)$$

$$V(G) = \frac{1}{L}\int_0^L dx\, V(x) \exp(-iGx) = \frac{1}{L} Aa \sum_{n=1}^{N} \exp(-iGna)\,, \quad G = integer \times \frac{2\pi}{a}$$

$$V(G) = \frac{1}{L} AaN = \frac{AL}{L} = A$$

$$N \to \infty$$

$$(\lambda_k - E)C(k) + A \sum_{n=-\infty}^{\infty} C\left(k - \frac{2\pi n}{a}\right) = 0$$

$$f(k) \equiv \sum_{n=-\infty}^{\infty} C\left(k - \frac{2\pi n}{a}\right)$$

$$C(k) = -\frac{Af(k)}{\lambda_k - E}$$

$$f\left(k - \frac{2\pi m}{a}\right) = f(k), \qquad m = any\ integer$$

$$f(k) = \sum_{n=-\infty}^{\infty} C\left(k - \frac{2\pi n}{a}\right) = \sum_{n=-\infty}^{\infty} -\frac{Af(k)}{\lambda_{k-2\pi n/a} - E}$$

$$1 = -\sum_{n=-\infty}^{\infty} \frac{A}{\lambda_{k-2\pi n/a} - E}$$

$$E = \frac{\hbar^2 K^2}{2m}$$

$$A = \frac{\hbar^2 P^2}{2m}$$

$$\cot(x) = \sum_{n=-\infty}^{\infty} \frac{1}{n\pi + x}$$

a bit of math

$$\frac{\hbar^2}{2mA} = -\sum_{n=1}^{N} \frac{1}{\left(k - \frac{2\pi n}{a}\right)^2 - K^2} = \frac{a^2 \sin(Ka)}{4Ka(\cos(ka) - \cos(Ka))}$$

$$\boxed{\frac{P \sin(Ka)}{Ka} + \cos(Ka) = \cos(ka)}$$

$$P = \frac{mAa^2}{2\hbar^2}$$

Toy Problem (Kronig-Penney)

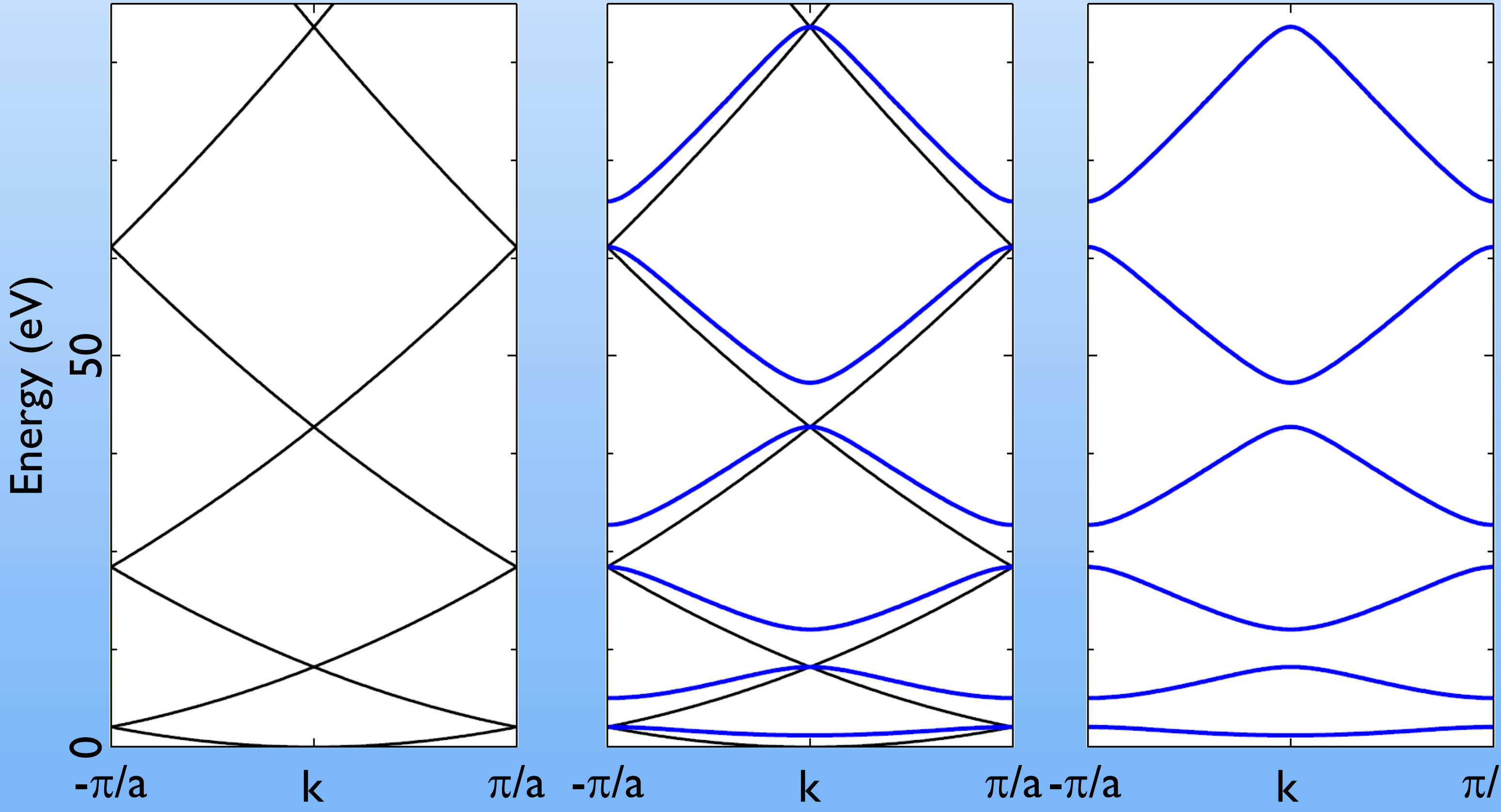
Note: G is reciprocal lattice vector here.

$$\frac{P\sin(Ka)}{Ka} + \cos(Ka) = \cos(ka)$$

$$P = \frac{mAa^2}{2\hbar^2}$$

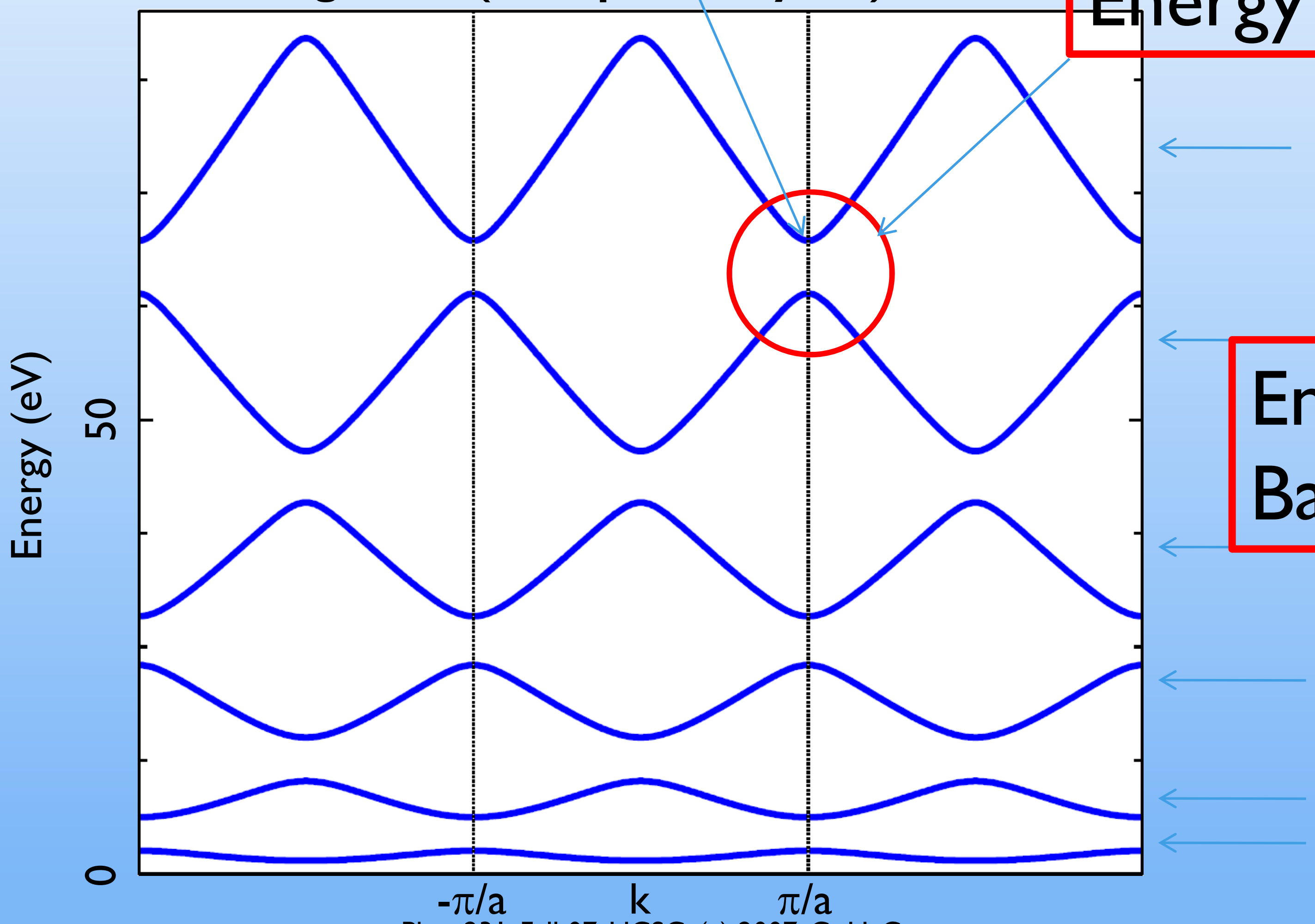
a=3.83Å

P = 6



Toy Problem (Kronig-Penney)

Standing Wave (Group velocity = 0)



Energy Gap

Energy Bands

Reminder

Consider a Hamiltonian for two states |0>, |1> interacting with each other

$$\begin{bmatrix} 0 & V \\ V^* & 0 \end{bmatrix}$$

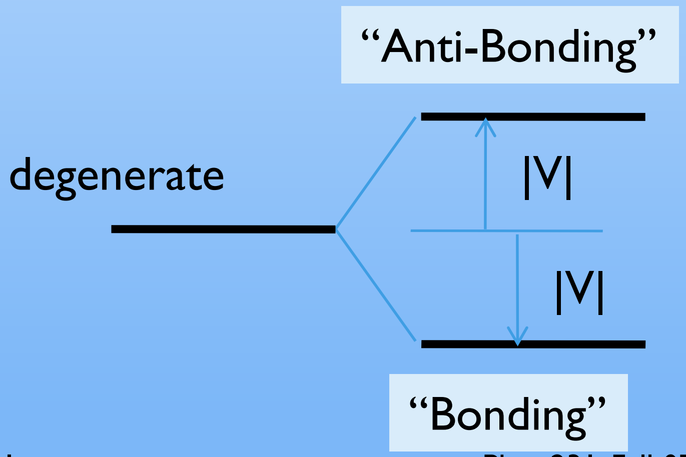
$V=|V|\exp(i\delta)$

Eigen-values = ± |V|

Equal parts of |0> and |1>

Eigen-state = $|0\rangle - \exp(-i\delta)|1\rangle$, for Eigen-value = -|V| (ground state)
$|0\rangle + \exp(i\delta)|1\rangle$, for Eigen-value = |V| (excited state)

Up to a normalization factor (1/sqrt(2))


"Anti-Bonding"

degenerate

"Bonding"

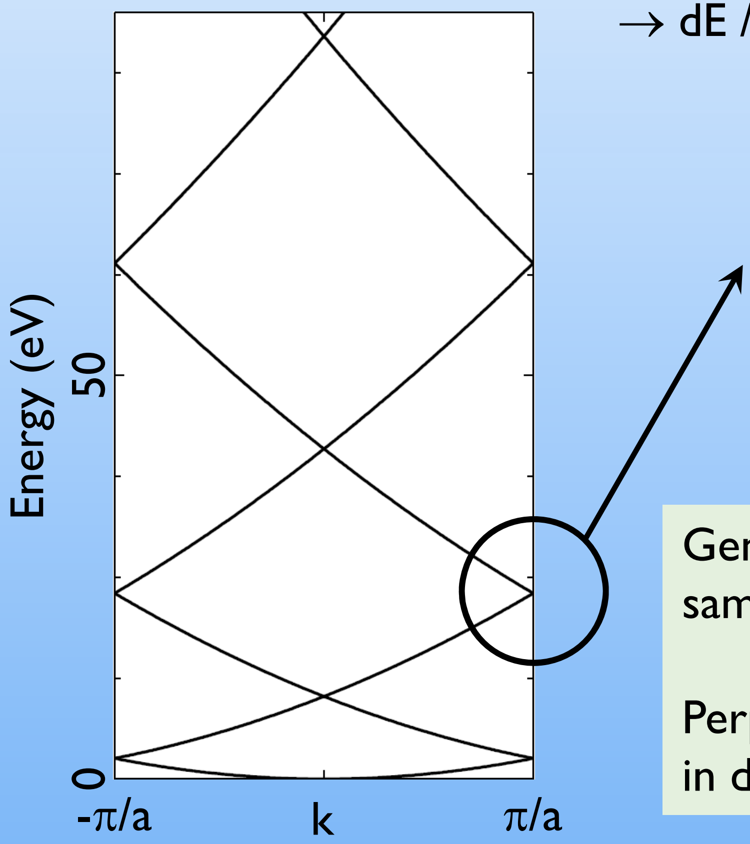
V real negative ($\delta=\pi$)	V real positive ($\delta=0$)
|0> -|1>	|0> +|1>
|0> +|1>	|0> -|1>

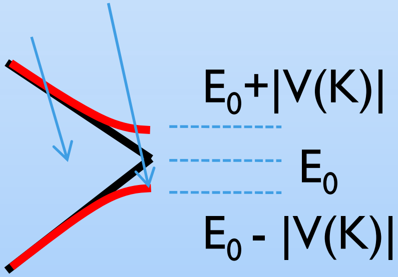
In the limit of weak potential (2x2 approx)

At $k=\pi/a$, wave function is equal mix of k and k+K

→ Standing Wave (group velocity = 0)

→ $dE / dk = 0$



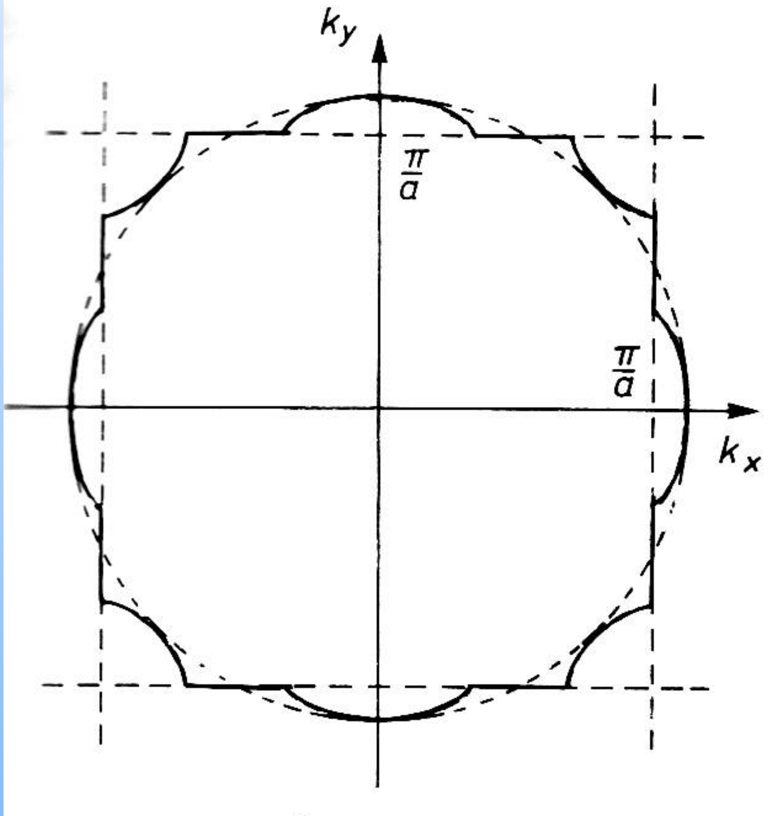


General condition that energies are the same

$$|\mathbf{k}| = |\mathbf{k}-\mathbf{K}|$$

Perpendicular bi-sector planes that we used in defining the BZ (Wigner Seitz Cell)!

Change in the Fermi Surface



Gradient of E(k) is parallel to the BZ face, i.e. the group velocity perpendicular to the BZ face is zero.

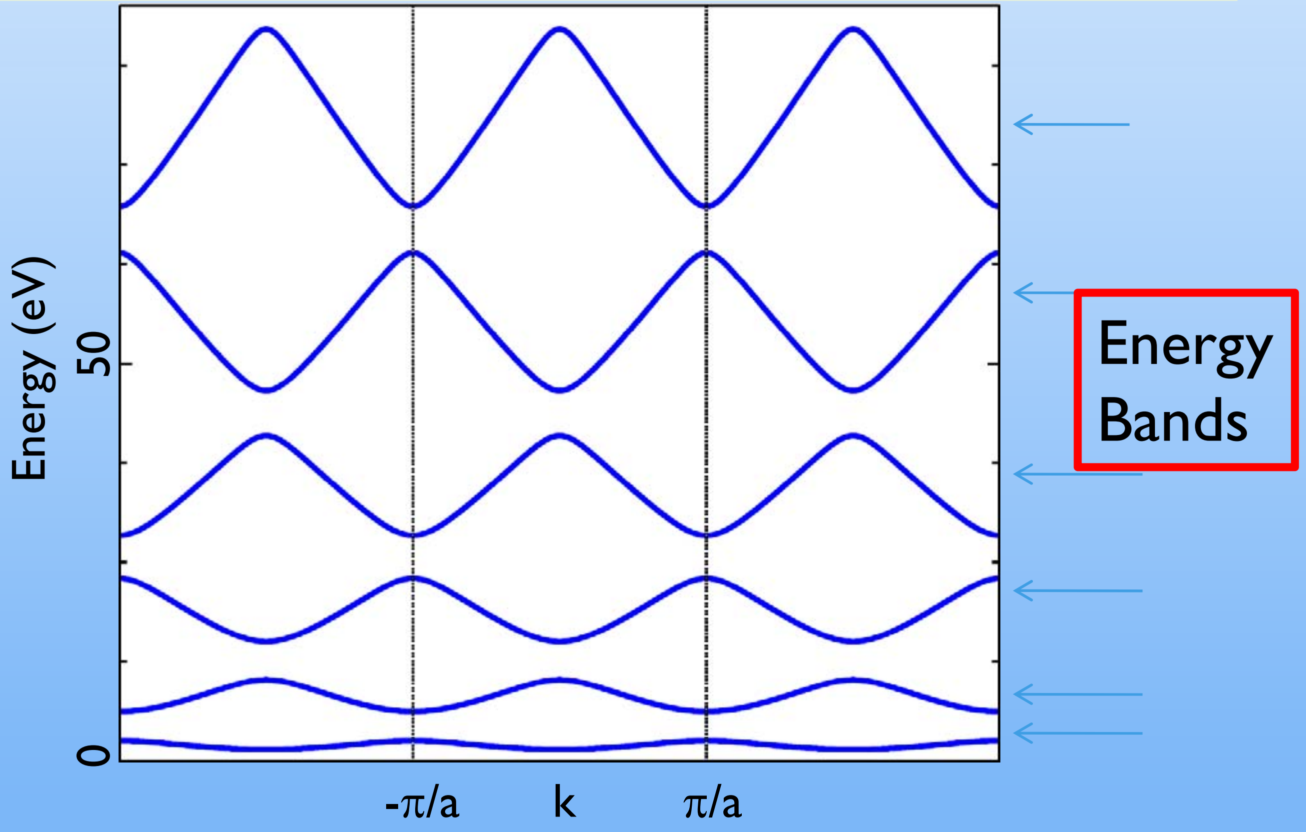
Constant energy contour intersects BZ at right angle

Metals, Insulator, Semi-conductors, Semi-metals

No band gap,	Gap >~ 1 eV,	Gap <~ 1 eV,	No Gap
Partially filled bands	All bands filled		Small number of e^-s and holes
T=0 FS	No T=0 FS		No or very small T=0 FS

To entirely fill a band, need 2 electrons per unit cell. Bands can also overlap.

Wilson's rule: metal if an odd number of free electrons per unit cell



Energy Bands

Tight Binding Method

(aka LCAO method, linear combination of atomic orbital)

- Another way of introducing the electron band concept, complimentary to the free electron view discussed so far
- Start from the atomic orbitals and construct electron band s by bonding and anti-bonding
- Equivalent to the free electron + crystal potential view
- Useful to think in terms of tight binding when orbitals are localized tightly around atomic cores (e.g. *d* or *f* orbitals in TM or RE ions) while it is useful to think in terms of free electron like band when orbitals are extended (e.g. *s* or *p* orbitals)

Motivation for Tight Binding Method

“Standard” View of Bloch’s Theorem

$$\psi_k(x) = \sum_K C(k+K)\exp(i(k+K)x) = \exp(ikx)\, u_k(x)$$

$\psi_k(x)$ is a linear combination of plane waves

$u_k(x)$ is the resulting modulation of the free electron wave function $\exp(ikx)$

Alternative View of Bloch’s Theorem

$$\psi_k(x) = \sum_R \exp(ikR)\ \phi(x-R)$$

Here R is index for lattice vectors, as G is index for reciprocal lattice vectors above.

It is easy to see that $\psi_k(x+R') = \exp(ikR')\psi_k(x)$ for any lattice vector R', and thus this is a legitimate way of writing the Bloch wave function.

In this view, the Bloch wave function can be viewed as a linear combination, with appropriate phase factors, of all “local” wave functions $\phi(x)$ – generally called “Wannier orbitals.”

Note: The 2nd way of writing the wave function is quite similar to what we did for lattice vibrations.
Lattice – assign a number (or several numbers); Electron – assign Wannier wave function.

Principle of Tight Binding Method

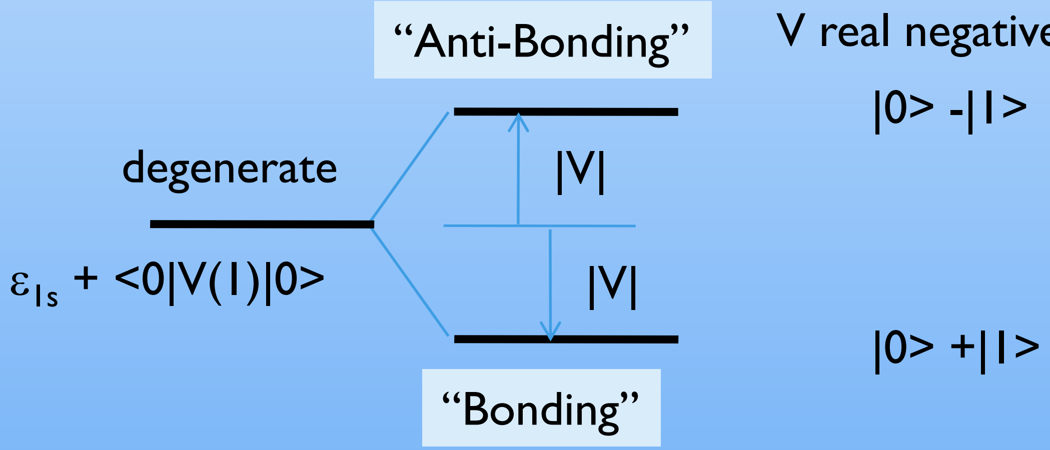
- Construct Wannier function from atomic orbitals
- To be precise in general, we need an infinite number of atomic orbitals
- Approximately, though, one can take a few atomic orbitals
- By choice, the matrix to diagonalize for each k has dimensions N x N, where N = sum of the number of atomic orbitals considered per each atom of the primitive basis

Practical Tight Binding Method

Fit the observed or the calculated band structure in order to encapsulate physics in simple terms

Simple Example of Tight Binding Method

- Consider only 1s orbitals for 1D crystal of hydrogen (hypothetical crystal – actually useful "toy model" for investigating transition metal or rare earth compounds)
- First consider a hydrogen molecule



"Anti-Bonding"

degenerate

ε_{1s} + <0|V(1)|0>

|V|

|V|

"Bonding"

V real negative

|0> -|1>

|0> +|1>

|0> : 1s wave function on one hydrogen atom

|1>: 1s wave function on the other hydrogen atom

V: Off-diagonal element of Hamiltonian

V = ε_{1s} <0|1> + <0|V(1)|1>

V(1) = Coulomb potential from proton of hydrogen 1

Simple and Useful Picture

- Of the two terms in V, consider only the 2nd term (we will call this –t), ignoring the 1st term, which tends to be smaller than the 1st term ("Wannier orbital"). Only in this case, the normalization factor of the bonding or anti-bonding wave function is $1/\sqrt{2}$.
- Consider a macroscopic 1D crystal consisting of $N = 2^M$ hydrogen atoms – one can consider bonding and anti-bonding of 2, 4, 6, 8, atoms in succession.
- N degenerate 1s orbitals split into states forming an "energy band" of width $= 2(t+t/2+t/4+\ldots) = 4t$
- For $t > 0$, then the lowest energy state $= 1/\sqrt{N}\,(|0\rangle+|1\rangle+\ldots|N-1\rangle)$ while the highest energy state $= 1/\sqrt{N}\,(|0\rangle-|1\rangle+|2\rangle-|3\rangle+\ldots|N-1\rangle)$. I.e., the lowest energy has $k=0$ while the highest energy has $k=\pi/a$.

Actual Solution of the 1s Tight Binding Model in 1D

$\varepsilon_k = \varepsilon_{1s} - 2\beta - 2t \cos(ka)$

$\beta = -\langle 0| V(1) |0\rangle$

$t = -\langle 0|V(1)|1\rangle$

$\langle 0|1\rangle$ is approximated as 0

This form is consistent with the consideration of the previous slide.

Bare Bone Tight Binding of H 1s

$H = T + V$ V: periodic pot.

$$|\psi\rangle = \sum_n e^{ikna}\,|n\rangle$$

$\langle n|H|n\rangle \equiv \varepsilon$ (throw in atomic energy -2β and so on)

$\langle m|H|n\rangle = -t$ if $m - n = \pm 1$

(keep nearest neighbor only)

t is called a "hopping" matrix element

$\langle m|n\rangle = \delta_{mn}$ (somewhat of a over-simplification but an often-used approx)

$$H\,|\psi\rangle = \varepsilon_k\,|\psi\rangle$$

$$\Downarrow \qquad\qquad \searrow$$

$$\langle m|H|\psi\rangle \qquad e^{ikna}\,\varepsilon_k$$

$$\boxed{\varepsilon_k = \varepsilon - 2t\cos ka}$$