Lecture 6

Electrons in Crystal

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

Review of the previous class

Q1: For electron gas, what is the temperature dependence of specific heat at low temperature (<< Fermi temperature)?

A. T B. T^2 C. T^3

Q2: For electron gas in 1D, what is the temperature dependence of specific heat at low temperature (<< Fermi temperature)?

A. T B. T^2 C. T^3

Q3: For electron gas with a dispersion relation, $\varepsilon(k) = k^{1/2}$, what is the temperature dependence of specific heat at low temperature (<< Fermi temperature)?

A. T B. T^2 C. T^3

Q4: Typical Fermi temperature of metals is

A. 100 K B. 10,000 K C. 10,000,000 K

Review of the previous class

Q5: For electron gas, which of the following is largely determined by the ground state (T=0) property?

A. Chemical potential B. Heat capacity C. Thermal Expansion

Q6: For electron gas, which of the following is strictly finite temperature property?

A. Bulk modulus B. Conductivity C. Thermal conductivity

Q7: Typical Fermi velocity of metals is NOT (c: speed of light, v_s = velocity of Debye phonon)

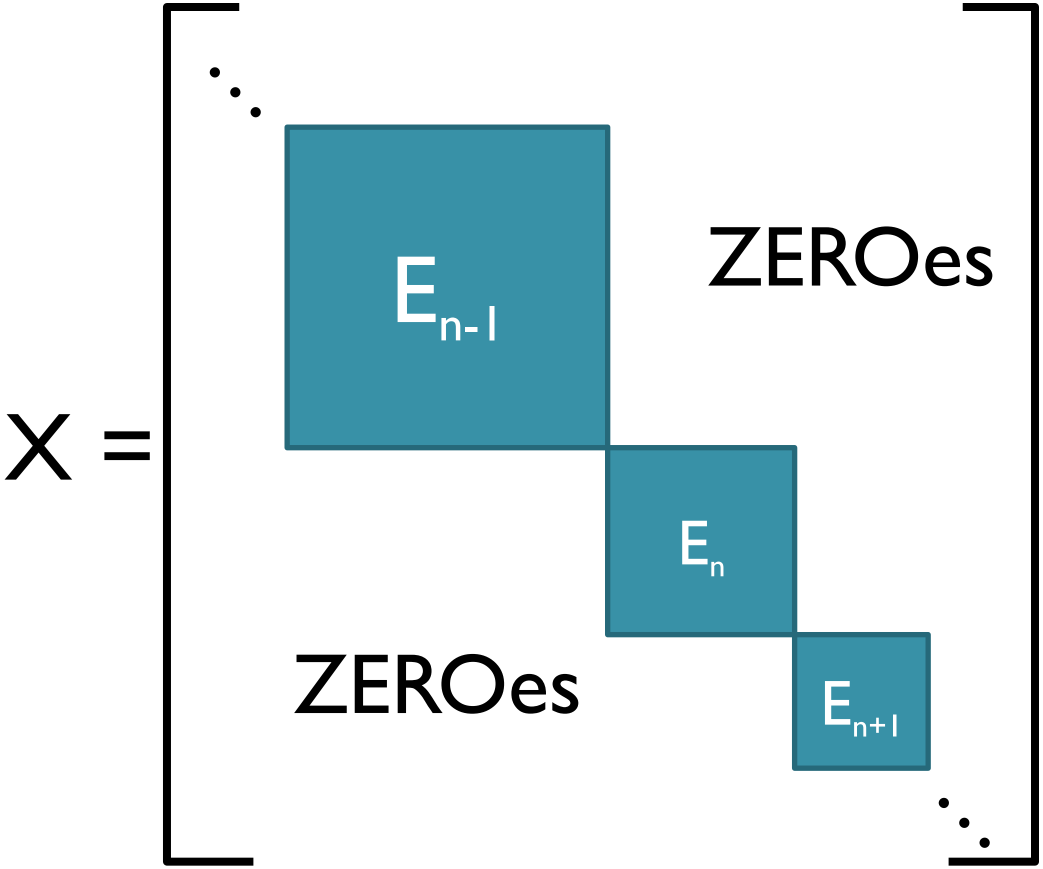
A. c/100 B. v_s C. v_s / 100

Q8: Current in metals propagates at the

A. speed of light B. Fermi velocity C. drift velocity (~ 1mm/s)

Prelude to Bloch's Theorem

$[H, X] = 0 \qquad HX|E\rangle = XH|E\rangle = EX|E\rangle$



When X can be diagonalized with a complete basis, then
<u>X and H can be simultaneously diagonalized</u> (see note).

Bloch's Theorem

For crystal translation $T_{\mathbf{R}}$, the complete basis can be taken as

$$\psi(\mathbf{x}) = \Sigma_{\mathbf{G}}\, C(\mathbf{k}+\mathbf{G}) \exp(i\,(\mathbf{k}+\mathbf{G})\cdot\mathbf{x})$$

C = complex number, **G** = reciprocal lattice vector

Bragg Diffraction Physics

Bloch's theorem (form 1):

The eigenstates of a periodic Hamiltonian can be chosen so that each eigenstate $\psi(\mathbf{x})$ satisfies:

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

where $u_{\mathrm{n}\mathbf{k}}(\mathbf{x})$ has the same periodicity as the Hamiltonian, i.e.

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

for any lattice vector $\mathbf{R}$ of the Hamiltonian. ($\hbar\mathbf{k}$ is crystal momentum – NOT true momentum – and n is symbol for all other quantum numbers – e.g. phonon branch in the case of phonons and band index, spin in the case of electrons)

Bloch's theorem (form 2):

The eigenstates of a periodic Hamiltonian can be chosen so that each eigenstate $\psi(\mathbf{x})$ satisfies:

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

for any lattice vector $\mathbf{R}$ of the Hamiltonian.

Never forget …

Q1: A potential is periodic with period a on a ring of length L. Wave vectors associated with the potential are:

A. integer x $2\pi/a$
B. integer x $2\pi/L$
C. any

Q2: For a phonon excitation on a 1D crystal of period a and length L, wave vectors are (within the Born-von-Karman B.C.):

A. discrete with increment $2\pi/a$
B. discrete with increment $2\pi/L$
C. continuous

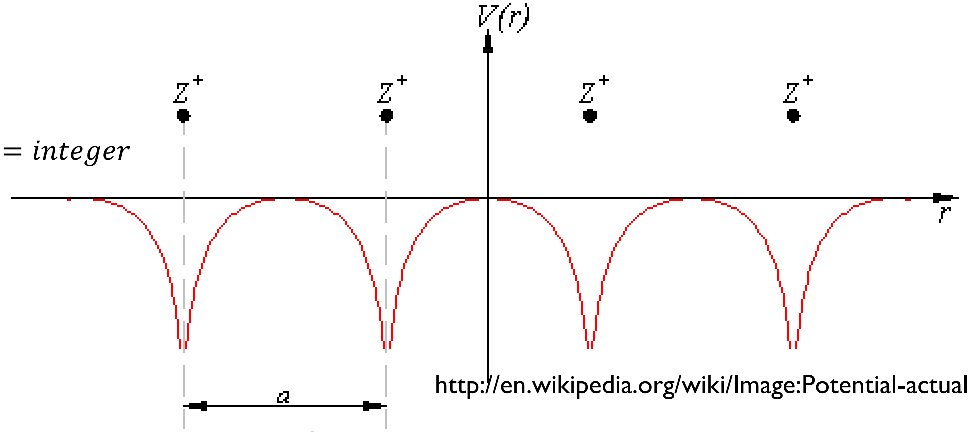
Q3: For electron or neutron on a 1D crystal of period a and length L, wave vectors are (within the Born-von-Karman B.C.):

A. discrete with increment $2\pi/a$
B. discrete with increment $2\pi/L$
C. continuous

Properties of Periodic Potential

$V(x+na) = V(x)$ for any integer n

$$\int_0^L dx V(x)\exp(-ikx) = 0 \quad \text{unless} \quad k = \frac{2\pi}{a} m, m = integer$$



http://en.wikipedia.org/wiki/Image:Potential-actual.PNG

proof

$$I \equiv \int_0^L dx V(x)\exp(-ikx)$$

$$I * \exp\,(ikna) \equiv \int_0^L dx V(x)\exp(-ik\,(x-na)) = \int_{-na}^{L-na} dx V(x+na)\exp(-ikx) = \int_{-na}^{L-na} dx V(x)\exp(-ikx) = I$$

In order for this true for any n, $k = \frac{2\pi}{a} \times integer \equiv G$ (reciprocal lattice vector

$$\boxed{V(x) = \sum_G V_G \exp(iGx)\,, \quad G = \frac{2\pi}{a} m, \quad m = integer}$$

$$V_G = \frac{1}{L}\int_0^L dx\, V(x)\exp(-iGx)$$

proof (if necessary)

$$\int_0^L dx\, V(x)\exp(-iG'x) = \sum_G V_G \int_0^L dx\, \exp(iGx)\exp(-iG'x) = \sum_G V_G\, L\delta_{G,G'} = LV_{G'}$$

$$\boxed{V(x) \text{ is real} \rightarrow V_G^* = V_{-G}}$$

Hamiltonian is Hermitian in plane wave basis – it should be.

Easy to generalize to 3D

$$V(\boldsymbol{x}) = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} \exp(i\boldsymbol{G}\cdot\boldsymbol{x})\,, \quad \boldsymbol{G} = p\boldsymbol{a}^* + q\boldsymbol{b}^* + r\boldsymbol{c}^*, \quad p,q,r = integers$$

$\boldsymbol{a},\boldsymbol{b},\boldsymbol{c} = real\ lattice \qquad \boldsymbol{a}^*,\boldsymbol{b}^*,\boldsymbol{c}^* = reciprocal\ lattice$

$$\boldsymbol{a}^*\cdot\boldsymbol{a} = \boldsymbol{b}^*\cdot\boldsymbol{b} = \boldsymbol{c}^*\cdot\boldsymbol{c} = 2\pi, \qquad \boldsymbol{a}^*\cdot\boldsymbol{b} = \boldsymbol{a}^*\cdot\boldsymbol{c} = \boldsymbol{b}^*\cdot\boldsymbol{c} = \boldsymbol{b}^*\cdot\boldsymbol{a} = \boldsymbol{c}^*\cdot\boldsymbol{a} = \boldsymbol{c}^*\cdot\boldsymbol{b} = 0$$

$$V_{\boldsymbol{G}}^* = V_{-\boldsymbol{G}}$$

Effect of Periodic Potential on Plane Wave Basis

$$\phi_k(x) = \exp(ikx)\,, \qquad k = \frac{2\pi}{L} \times integer \ \ (\text{Born} - \text{von Karman B.C.})$$

$$H = \frac{p^2}{2m} + V(x)$$

for k≠k'

$$\langle \phi_{k'} | H | \phi_k \rangle = \langle \phi_{k'} | V | \phi_k \rangle = \int_0^L dx \exp(i(k-k')x)\, V(x)$$

$$V(x) = \sum_G V_G \exp(iGx)\,, \ \ G = \frac{2\pi}{a} m, \ \ m = integer$$

$$\langle \phi_{k'} | H | \phi_k \rangle = \sum_G V_G \int_0^L dx \ \exp(i(G+k-k')x)$$

$$G + k - k' = \frac{2\pi}{a} \times integer + \frac{2\pi}{L} \times integer = \frac{2\pi}{L} \times integer \qquad Period = \frac{L}{integer}$$

$$\langle \phi_{k'} | H | \phi_k \rangle = 0 \ \text{ unless } \ k - k' = G \ (\text{any reciprocal lattice vector})$$

$$\psi_k(x) = \sum_G C(k+G) \exp(i(k+G)x) = \exp(ikx)\, u_k(x)$$

$$u_k(x + na) = u_k(x)$$

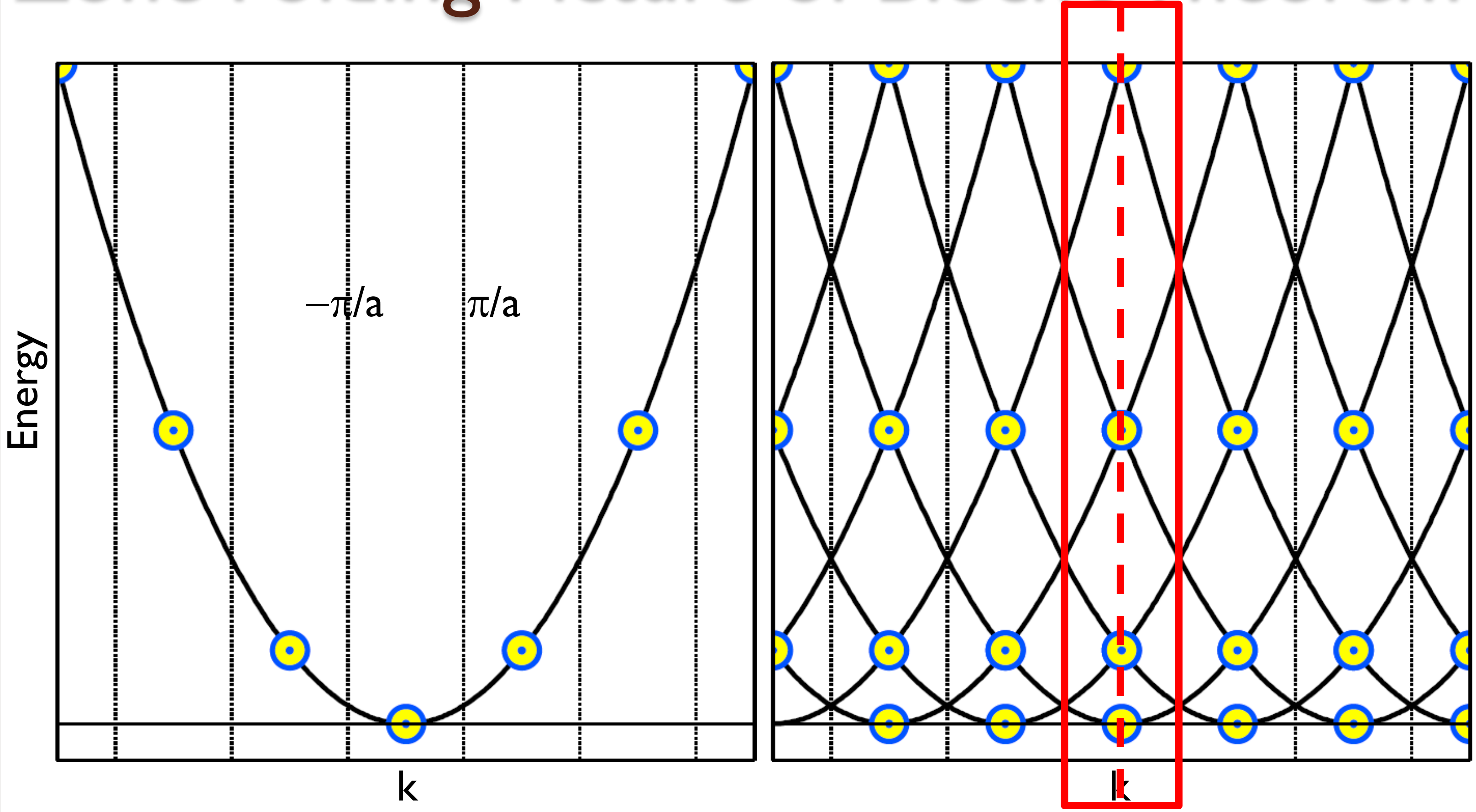
$$\psi_k(x + na) = \exp(ikna)\, \psi_k(x)$$

Another proof of Bloch's theorem

Easily generalized to 3D

(other quantum numbers such as spin are implicit)

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

VERY IMPORTANT

Crystal Momentum

- Just like in phonon case, the wave vector k is ambiguous up to any reciprocal lattice vector

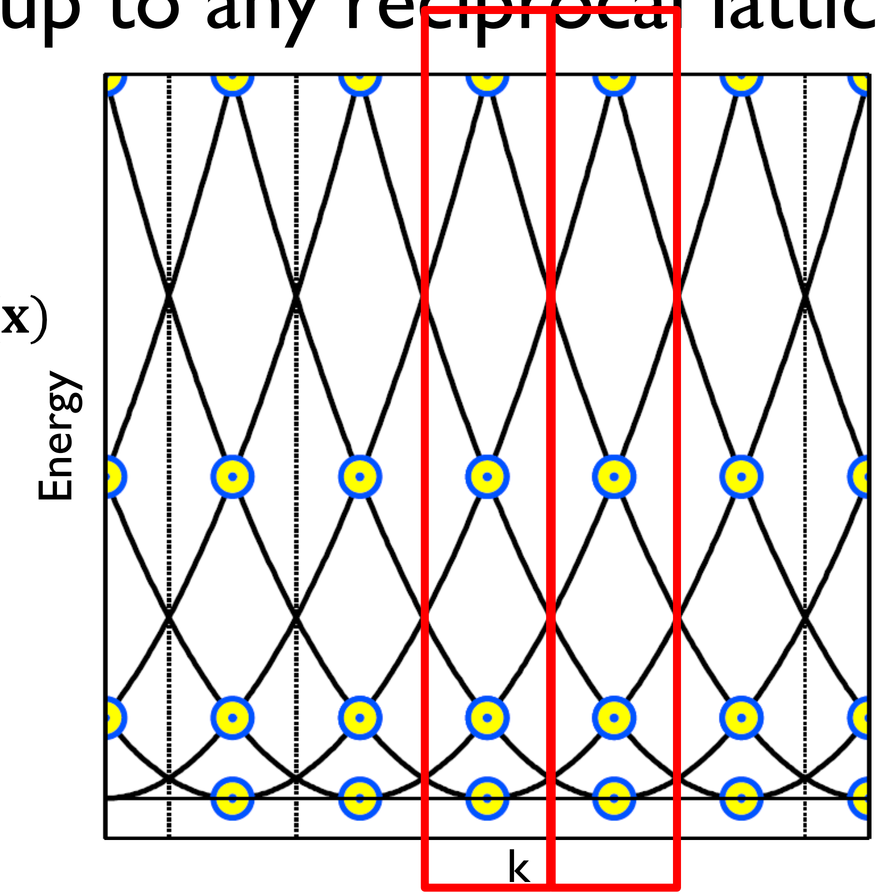
$$\psi_{\mathbf{nk}}(\mathbf{x}+\mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R})\,\psi_{\mathbf{nk}}(\mathbf{x})$$

$\uparrow$

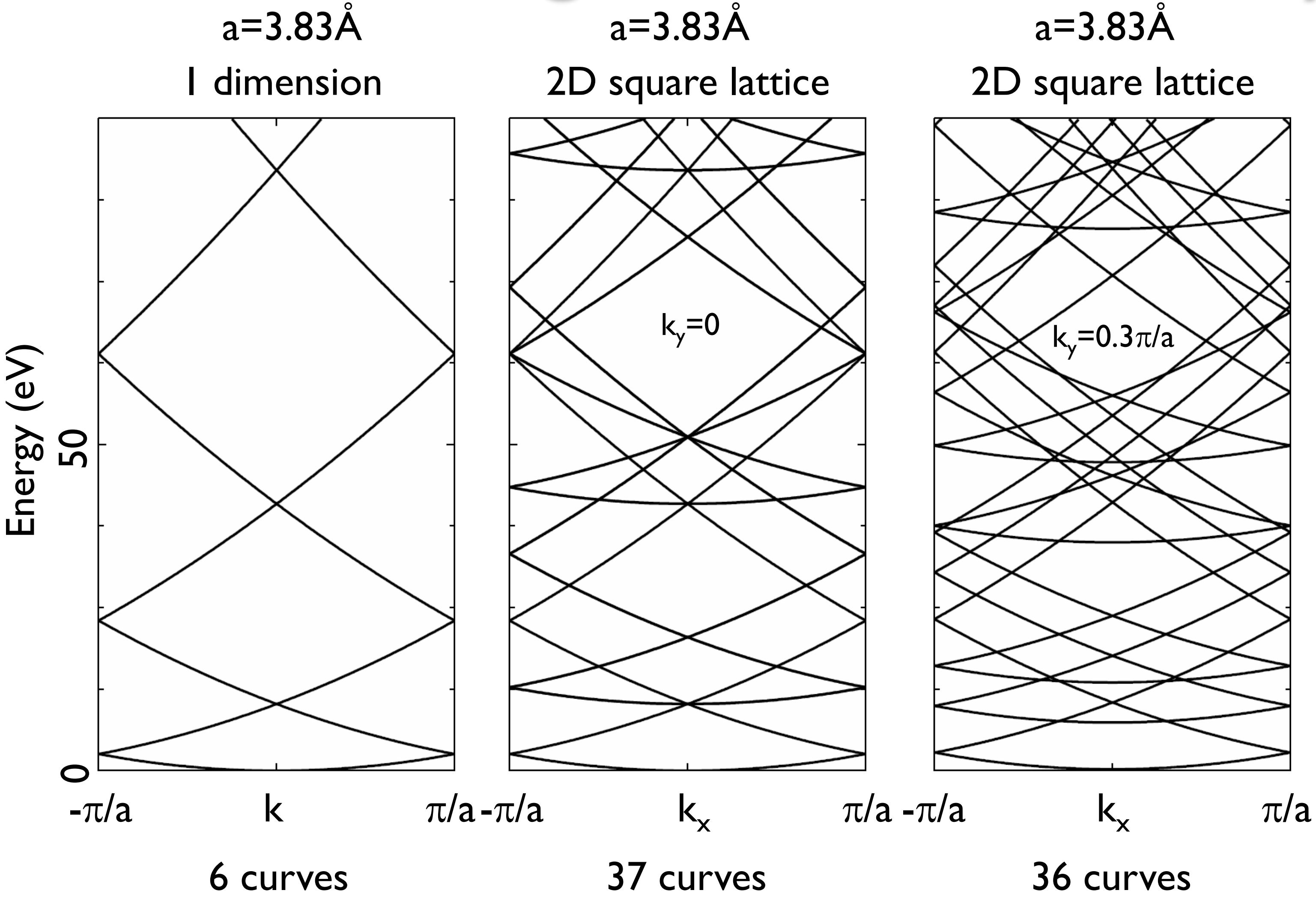
Eigen-value of lattice translation

k is "**crystal momentum**"

ambigous up to **G**

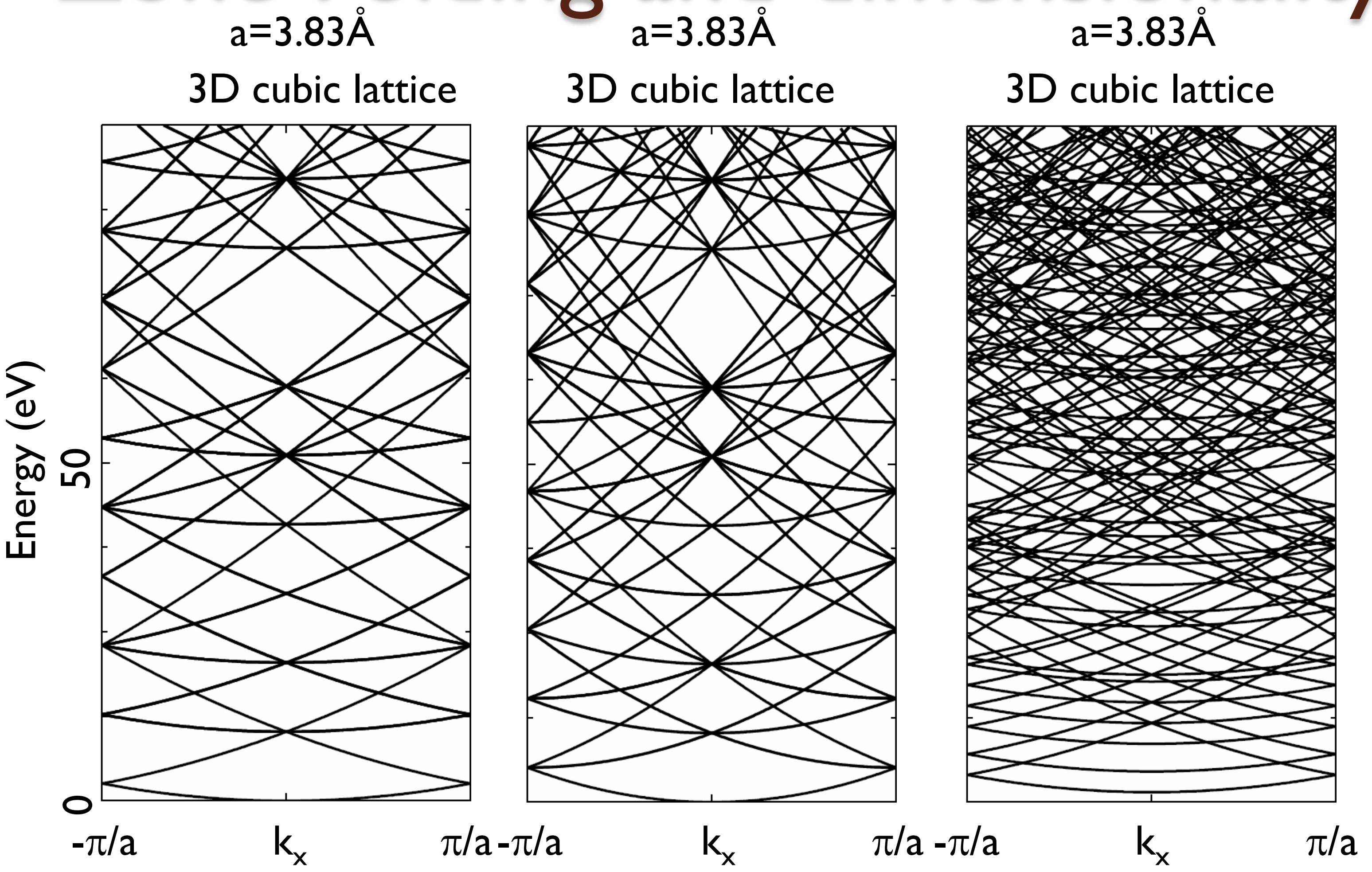


Zone-Folding and dimensionality



Zone-Folding and dimensionality

This is what makes the scattering, such as photoelectric effect, possible in crystal, while it may not be possible in free space (homework).


a=3.83Å
3D cubic lattice
a=3.83Å
3D cubic lattice
a=3.83Å
3D cubic lattice

$k_y=k_z=0$
147 curves

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

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

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

Equation of Motion (∞ x ∞)

$$H = \frac{p^2}{2m} + V(x) = \frac{p^2}{2m} + \sum_G V(G)\exp(iGx)$$

$$\psi_k(x) = \sum_{G'} C(k+G')\exp(i(k+G')x)$$

$$H\psi_k(x) = \sum_{G'} \lambda_{k+G'} C(k+G')\exp(i(k+G')x) + \sum_{G,G'} V(G)\exp(iGx)\, C(k+G')\exp(i(k+G')x)$$

$$\lambda_k = \frac{\hbar^2 k^2}{2m}$$

$$H\psi_k(x) = \sum_{G'} \lambda_{k+G'} C(k+G')\exp(i(k+G')x) + \sum_{G,G'} V(G)\, C(k+G')\exp(i(k+G+G')x)$$

$$= \sum_{G'} \lambda_{k+G'} C(k+G')\exp(i(k+G')x) + \sum_{G,G'} V(G)\, C(k+G'-G)\exp(i(k+G')x)$$

$$= \sum_{G'} \left[\lambda_{k+G'} C(k+G') + \sum_G V(G)\, C(k+G'-G)\right]\exp(i(k+G')x)$$

∞ x ∞ matrix !

$$H\psi_k(x) = E\psi_k(x) = E\sum_{G'} C(k+G')\exp(i(k+G')x)$$

$$\lambda_{k+G'} C(k+G') + \sum_G V(G)\, C(k+G'-G) = EC(k+G')$$

$$(\lambda_{k+G'} - E)C(k+G') + \sum_G V(G)\, C(k+G'-G) = 0$$

$$\boxed{(\lambda_k - E)C(k) + \sum_G V(G)\, C(k-G) = 0}$$

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

Toy Problem (Kronig-Penney)

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

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

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

$$N \rightarrow \infty$$

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

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

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

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

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

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

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

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

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

a bit of math

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

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

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

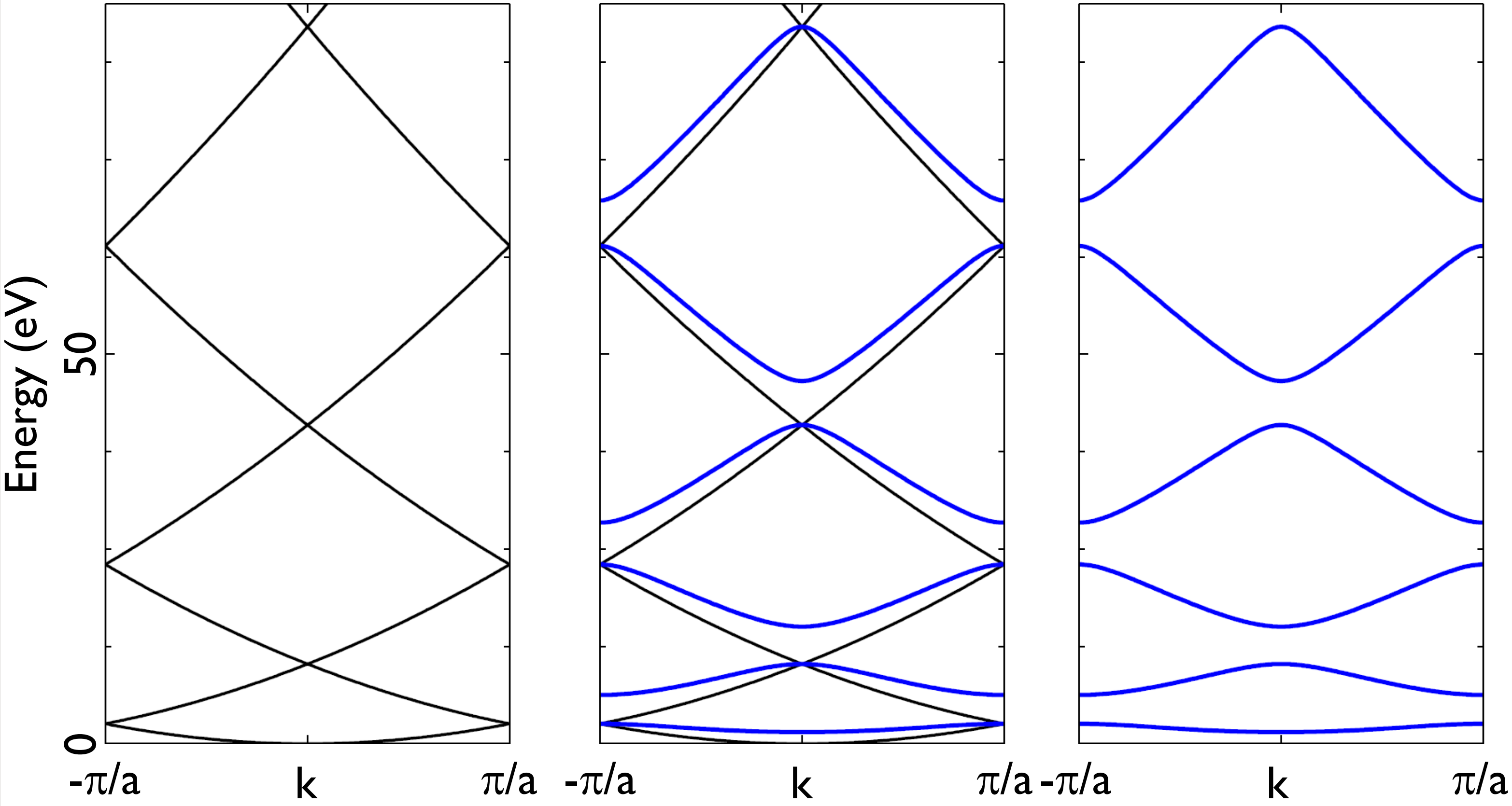
Toy Problem (Kronig-Penney)

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

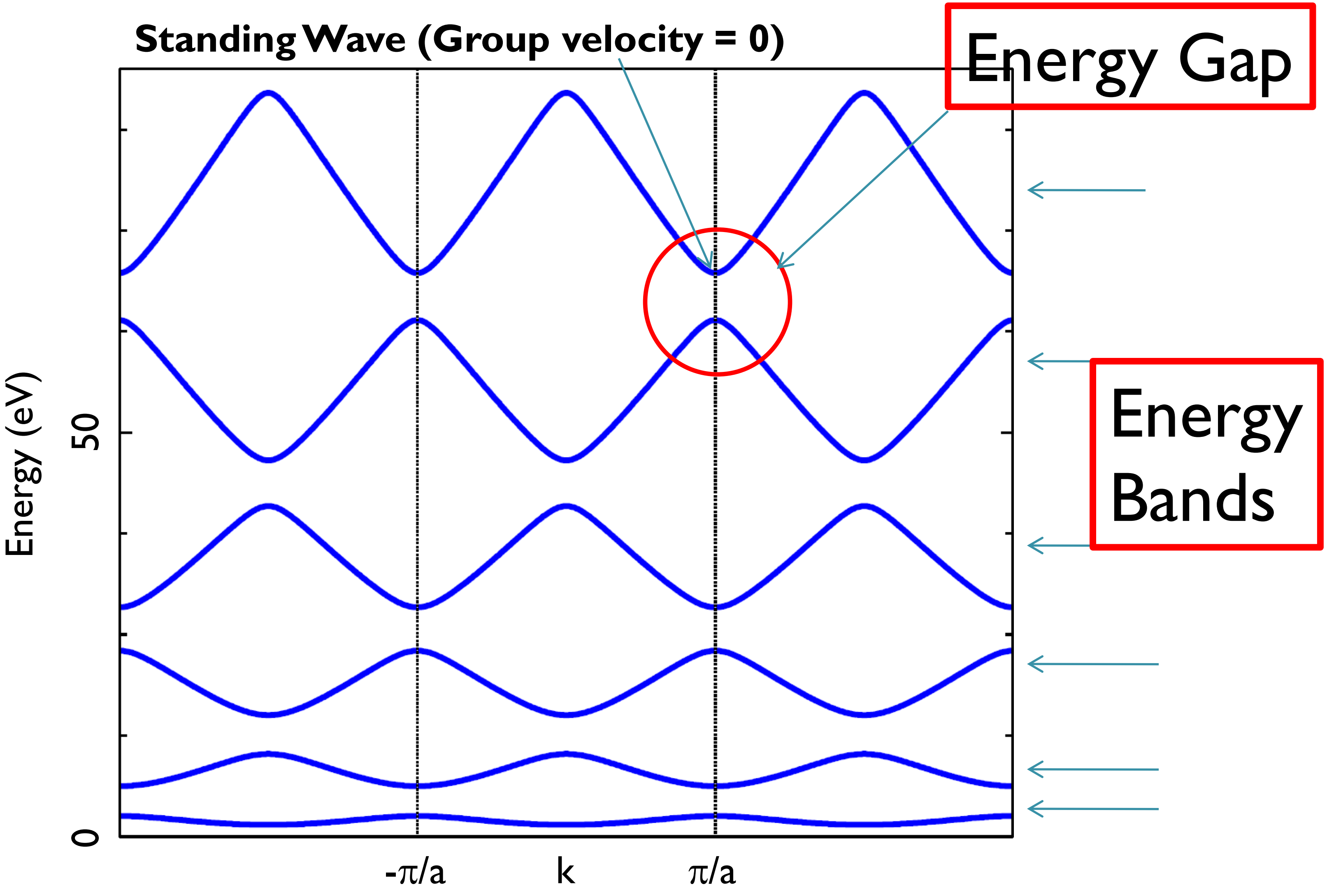
$$P=\frac{mAa^2}{2\hbar^2}$$

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

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

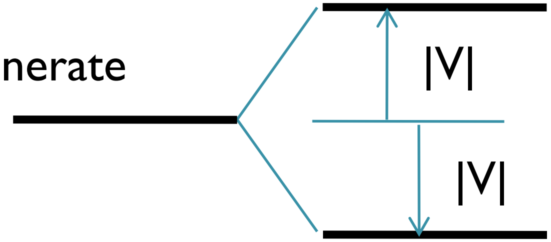
$V=|V|\exp(i\delta)$

Eigen-values = ± |V|

Equal parts of |0> and |1>

Eigen-state = |0> - exp(-iδ)|1>, for Eigen-value = -|V| (ground state)
|0> + exp (iδ) |1>, for Eigen-value = |V| (excited state)

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



"Anti-Bonding"

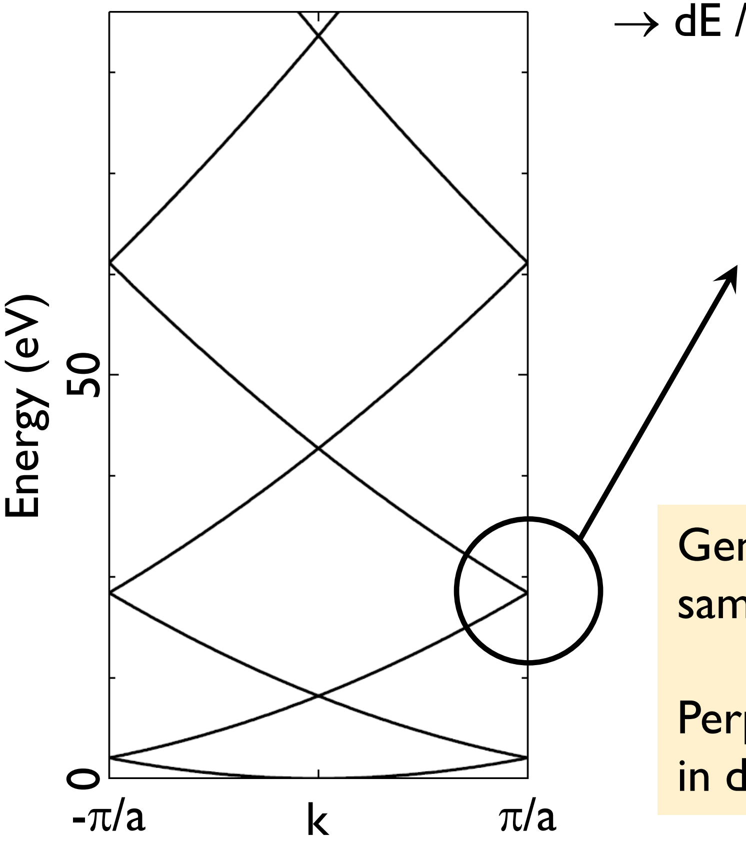
degenerate

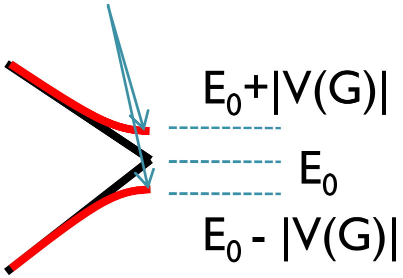
"Bonding"

V real negative (δ=π)	V real positive (δ=0)
|0> -|1>	|0> +|1>
|0> +|1>	|0> -|1>

In the limit of weak potential

At $k=\pi/a$, wave function is equal mix of k and k+G
→ Standing Wave (group velocity = 0)
→ $dE / dk = 0$



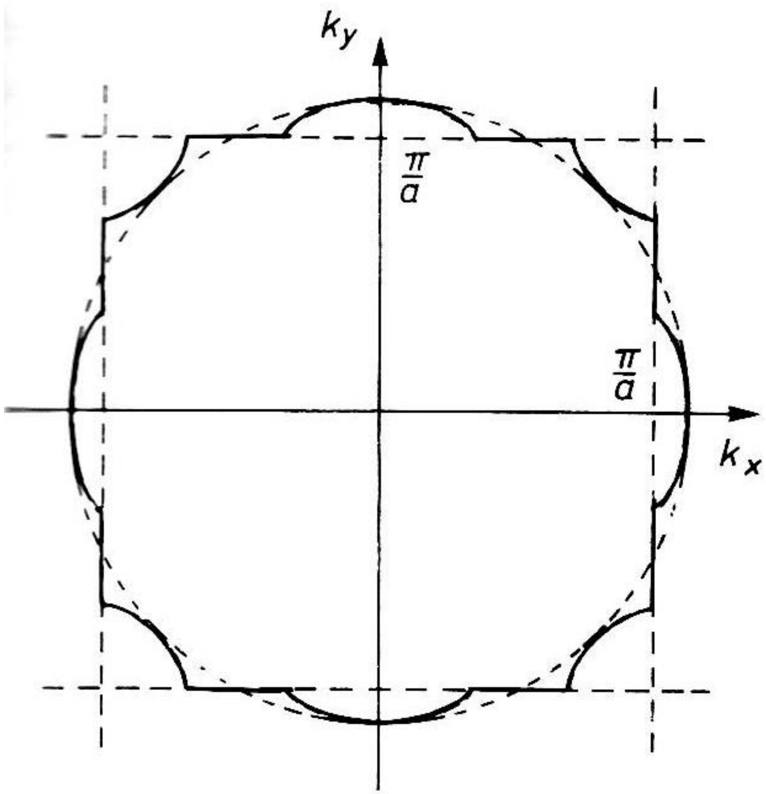


General condition that energies are the same

$$|\mathbf{k}| = |\mathbf{k}\text{-}\mathbf{G}|$$

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

Change in the Fermi Surface



H&H, Figure 4.5

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

Constant energy contour intersects BZ at right angle

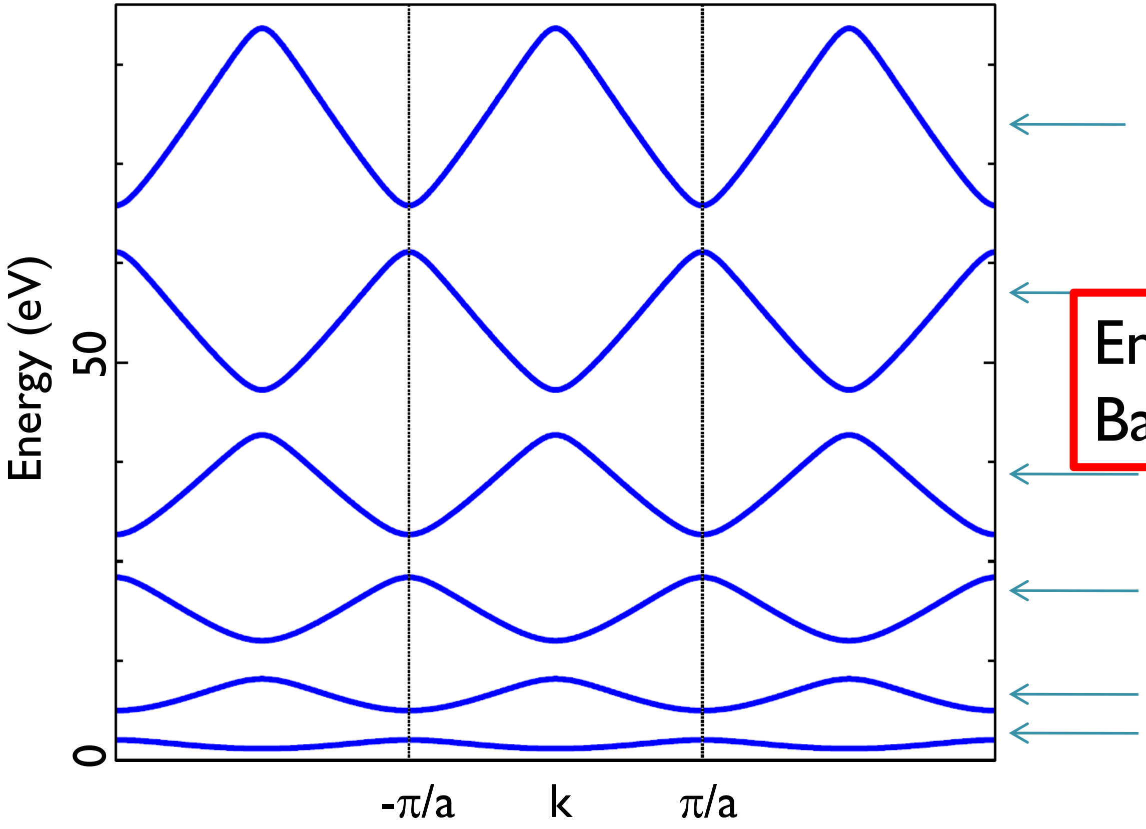
Metals, Insulator, Semi-conductors, Semi-metals

No band gap, Gap > 1 eV, Gap < 1 eV, No Gap

Partially filled bands All bands filled Small number of e$^-$s and holes

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

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 bands 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)

Note

Motivation for Tight Binding Method

- One View of Bloch's Theorem

$$\psi_k(x) = \sum_G C(k+G)\exp(i(k+G)x) = \exp(ikx)\,u_k(x)$$

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

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

- Another 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 phonons.
Phonon – assign a number (or several numbers); Electron – assign Wannier wave function.

Note

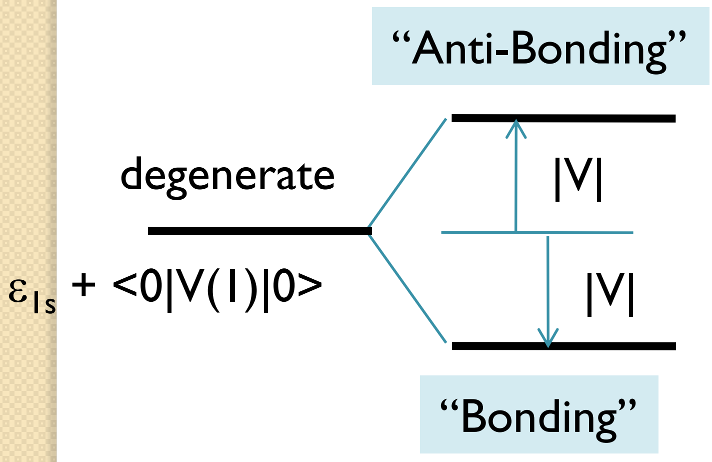
Tight Binding Method

- 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

Note

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 – recall from slide 17



"Anti-Bonding"

degenerate

$\varepsilon_{1s} + \langle 0|V(1)|0\rangle$

|V|

|V|

"Bonding"

V real negative

$|0\rangle - |1\rangle$

$|0\rangle + |1\rangle$

$|0\rangle$: 1s wave function on one hydrogen atom

$|1\rangle$: 1s wave function on the other hydrogen atom

V: Off-diagonal element of Hamiltonian

$V = \varepsilon_{1s} \langle 0|1\rangle + \langle 0|V(1)|1\rangle$

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

Note

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. 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 "energey 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 $k=\pi/a$.

Note

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

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

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

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

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

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

Note