

PHYS 460 LECTURE 10

IN THE LAST LECTURE, WE WERE DISCUSSING FAILURES OF THE FREE ELECTRON MODEL AND SAW HOW EVEN THE SIMPLEST OF MODIFICATIONS TO INCLUDE LATTICE EFFECTS EXPLAINED A HOST OF PHYSICAL PROPERTIES. SPECIFICALLY, WE SAW THAT EFFECT BRAGG SCATTERING OF ELECTRON WAVES OPENED GAPS IN THE AVAILABLE ENERGY LEVELS AT BRILLOUIN ZONE BOUNDARIES. THESE GAPS WERE ENOUGH TO EXPLAIN DIFFERENCES BETWEEN METALS AND INSULATORS AND WHY ELECTRONS IN A SOLID HAVE MASS DIFFERENT FROM BARE MASS (AND SOMETIMES $\neq$ CHARGE)!

WE ALSO SAW THOUGH THAT THE STRENGTH OF ELECTRON-ION INTERACTIONS IS SUCH THAT ~~THE~~ THE USE OF PERTURBATION THEORY IS VERY OFTEN NOT JUSTIFIED. SO IF THE FREE ELECTRON PICTURE IS NOT A GOOD PLACE TO START, HOW DO WE APPROACH THE PROBLEM OF ELECTRONS IN A PERIODIC POTENTIAL, AND WHY DID TREATING ELECTRONS AS TRAVELLING WAVES WORK SO WELL?

ANSWERS CAN BE FOUND IN BLOCH'S THEOREM:

THEOREM: THE EIGENSTATES $\psi(\vec{r})$, OF AN ELECTRON IN A PERIODIC POTENTIAL $U(\vec{r})$ WITH THE PROPERTY $U(\vec{r} + \vec{R}) = U(\vec{r})$, FOR $\vec{R}$ SOME BRAVAIS LATTICE, CAN ALWAYS BE WRITTEN

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r})$$

WHERE $u_{n\vec{k}}(\vec{r} + \vec{R}) = u_{n\vec{k}}(\vec{r})$

THAT IS, IN A PERIODIC POTENTIAL, THE EIGENSTATE OF AN ELECTRON CAN ALWAYS BE EXPRESSED AS A MODIFIED PLANK WAVE WITH A PERIODIC PREFACTOR.

HERE, JUST TO INTRODUCE SOME LANGUAGE

$\psi_{n,\vec{k}}$ = "MODIFIED PLANKWAVE" SOLUTION

$u_{n,\vec{k}}$ = "BLOCH FUNCTION"

$\hbar\vec{k}$ = CRYSTAL MOMENTUM, WHICH CAN ALWAYS BE CHOSEN TO BE IN 1st BZ

n = "BAND INDEX" AND REFLECT THE FACT THAT SOLUTIONS AT EACH $\vec{k}$ ARE NOT UNIQUE

NOTE THAT THE PERIODICITY OF $u_{n,\vec{k}}(\vec{r})$ IMPLIES THAT IT CAN BE EXPRESSED AS A SUM OF FOURIER COMPONENTS, $\vec{G}$ (THE RECIPROCAL LATTICE):

$$u_{n,\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{n,\vec{G}}(\vec{k}) e^{i\vec{G} \cdot \vec{r}}$$

$$\begin{aligned} \Rightarrow \psi_{n,\vec{k}}(\vec{r}) &= e^{i\vec{k} \cdot \vec{r}} \sum_{\vec{G}} u_{n,\vec{G}}(\vec{k}) e^{i\vec{G} \cdot \vec{r}} \\ &= \sum_{\vec{G}} u_{n,\vec{G}}(\vec{k}) e^{i(\vec{G} + \vec{k}) \cdot \vec{r}} \end{aligned}$$

$$\begin{aligned} \Rightarrow \psi_{n,\vec{k}}(\vec{r} + \vec{R}) &= \sum_{\vec{G}} u_{n,\vec{G}}(\vec{k}) e^{i(\vec{G} + \vec{k}) \cdot \vec{r}} e^{i(\vec{G} + \vec{k}) \cdot \vec{R}} \\ &= e^{i\vec{k} \cdot \vec{R}} \psi_{n,\vec{k}}(\vec{r}) \end{aligned}$$

since $e^{i\vec{G} \cdot \vec{R}} = 1$

WE CAN SHOW THAT THIS LATER IDENTITY IMPLIES THE FIRST BY REVERSING THE ARGUMENT. THUS, AN ALTERNATE STATEMENT OF BLOCH'S THEOREM IS THAT EIGENSTATES OF A PERIODIC POTENTIAL HAVE THE PROPERTY THAT

$$\boxed{\psi_{n,E}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{n,E}(\vec{r}) \quad \forall \vec{R}}$$

PROOF OF BLOCH'S THEOREM

CONSIDER THE TRANSLATION OPERATOR $T_{\vec{a}_j}$, DEFINED SUCH THAT

$$T_{\vec{a}_j} \psi(\vec{r}) = \psi(\vec{r} + \vec{a}_j)$$

FOR PRIMITIVE LATTICE VECTOR $\vec{a}_j$

APPLY TO OUR HAMILTONIAN

$$H(\vec{p}, \vec{r}) = \frac{p^2}{2m} + V(\vec{r})$$

$$\text{AND } H(\vec{p}, \vec{r}) \psi(\vec{r}) = E \psi(\vec{r})$$

$$\rightarrow T_{\vec{a}_j} \{ H(\vec{p}, \vec{r}) \psi(\vec{r}) \} = T_{\vec{a}_j} \{ E \psi(\vec{r}) \}$$

$$H(\vec{p}, \vec{r} + \vec{a}_j) \psi(\vec{r} + \vec{a}_j) = E \psi(\vec{r} + \vec{a}_j)$$

$$H(\vec{p}, \vec{r}) \psi(\vec{r} + \vec{a}_j) = E \psi(\vec{r} + \vec{a}_j)$$

$$H(\vec{r}, \vec{r}) T_j \psi(\vec{r}) = E T_j \psi(\vec{r})$$

OR ALL TOGETHER

$$T_j H \psi = H T_j \psi$$

$$[H, T_j] = 0 \quad H \text{ \& T_j \text{ commute}$$

AND THUS SHARE EIGENSTATES

LOOK FOR EIGENSTATES OF T_j :

$$\boxed{T_j \psi = \lambda_j \psi} \quad \text{DEFINITION OF } \psi$$

$$\Rightarrow T_j \psi(\vec{r}) = \psi(\vec{r} + \vec{a}_j) = \lambda_j \psi(\vec{r})$$

APPLY TWICE

$$T_j^2 \psi(\vec{r}) = \psi(\vec{r} + 2\vec{a}_j) = \lambda_j^2 \psi(\vec{r})$$

:

$$T_j^N \psi(\vec{r}) = \psi(\vec{r} + N\vec{a}_j) = \lambda_j^N \psi(\vec{r})$$

BUT IF N IS THE NUMBER OF UNIT CELLS IN DIRECTION j , PERIODIC BOUNDARY CONDITIONS IMPLY

$$\psi(\vec{r} + N\vec{a}_j) = \psi(\vec{r})$$

$$\Rightarrow \lambda_j^N = 1$$

$$\Rightarrow \lambda_j = e^{i\vec{k} \cdot \vec{a}_j}$$

FOR $\vec{k} = \frac{n\vec{b}_j}{N}$

RECIPROCAL
LATTICE
VECTOR

$$\therefore \boxed{\psi(\vec{r} + \vec{r}) = e^{i\vec{k} \cdot \vec{r}} \psi(\vec{r})}$$

QED

OK, THIS IS HUGE. EVEN FOR ARBITRARILY STRONG LATTICE INTERACTIONS, BLOCH'S THEOREM IMPLIES THAT ELECTRONS ARE STILL TRAVELLING WAVE-"ISIT". THERE ARE SOME PROPERTIES TO NOTE:

① EVEN THOUGH THE HAMILTONIAN IS INVARIANT UNDER TRANSLATIONS T_j , THE ELECTRON WAVEFUNCTION IS NOT! TRANSLATING WITHIN THE CRYSTAL GIVES THE ELECTRON WAVEFUNCTION AN ADDITIONAL PHASE FACTOR

$$e^{i\vec{k} \cdot \vec{R}}$$

② THESE WAVEFUNCTION ALSO HAVE A WAVEVECTOR $\vec{k}$ WHICH FOR FREE WAVES PLAYS THE ROLE OF MOMENTUM, $\hbar\vec{k}$

HOWEVER BLOCH WAVES DON'T DIAGONALIZE THE MOMENTUM OPERATOR

$$\begin{aligned} \hat{p} \psi_{n,\vec{k}} &= -i\hbar \vec{\nabla} \psi_{n,\vec{k}} = -i\hbar \vec{\nabla} (e^{i\vec{k} \cdot \vec{r}} u_{n,\vec{k}}) \\ &= \hbar\vec{k} e^{i\vec{k} \cdot \vec{r}} u_{n,\vec{k}} - i\hbar e^{i\vec{k} \cdot \vec{r}} \vec{\nabla} u_{n,\vec{k}} \\ &= \hbar\vec{k} \psi_{n,\vec{k}} + \text{SOMETHING ELSE} \end{aligned}$$

THESE WAVES DON'T HAVE WELL DEFINED MOMENTUM $\rightarrow \hbar\vec{k}$ IS "CRYSTAL MOMENTUM"

③ DESPITE THESE QUALIFIERS, WE STILL SEE THAT STATES ASSOCIATED WITH WAVEVECTOR $\vec{k}$ (a) ARE EQUALLY LIKELY TO HAVE ELECTRONS IN ALL UNIT CELLS OF THE CRYSTAL ($|u|^2$ DOESN'T DEPEND ON PHASE)

AND

(b) HAVE A FINITE VELOCITY

$$v_{n,\vec{k}} = \frac{1}{\hbar} \nabla_{\vec{k}} \epsilon_{n,\vec{k}}$$

IF $\epsilon_{n,\vec{k}}$ HAS ANY DISPERSION WHATSOEVER

THAT IS, ELECTRONS WITH APPROPRIATELY CHOSEN $\vec{k}$ CAN TRAVEL THROUGHOUT THE CRYSTAL WITHOUT DISSIPATION!!!

④ INVOKATION OF CRYSTAL MOMENTUM MAY REMIND US OF PHONONS, AND AS WITH PHONONS IT IS COMMON TO SHOW ENERGY LEVELS USING A "REDUCED ZONE SCHEME", WHEREIN STATES ARE PLOTTED IN THE FIRST BRILLOUIN ZONE BY SUBTRACTING OFF INTEGER VALUES OF RECIPROCAL LATTICE VECTORS

$$\vec{k}' = \vec{k} - \vec{G}$$

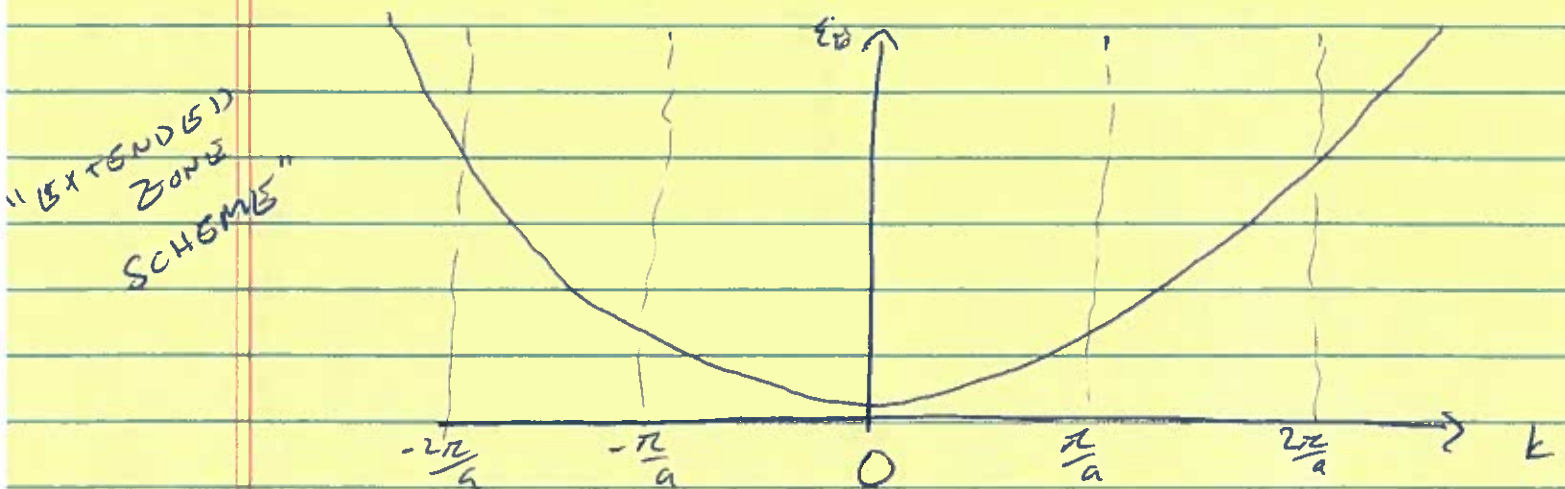
THIS ALLOWS US TO PLOT HIGHER $\vec{k}$ (AND ENERGY) MODES IN THE FIRST ZONE AND LABEL THEM WITH A BAND INDEX n

LET'S CLARIFY THIS LAST POINT WITH A SIMPLE EXAMPLE:

1D "EMPTY LATTICE" ($U=0$)

WE SEE THAT BLOCH WAVES IN THIS CASE SIMPLY REDUCE TO FREE WAVES ($U_E = 1$)

$$\rightarrow \psi_E = e^{i\vec{k} \cdot \vec{r}}, \quad E_E = \frac{\hbar^2 k^2}{2m}$$



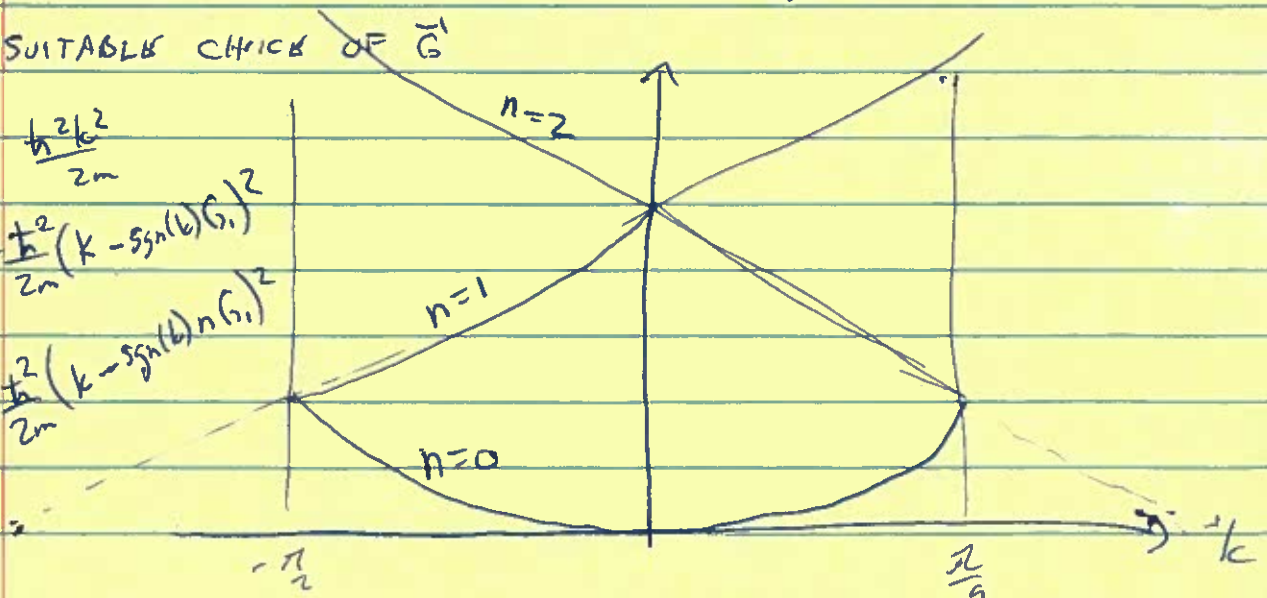
IN THE "REDUCED ZONE SCHEME" ONE CAN REPLOT BY SHIFTING ANYTHING ~~OUT~~ OUTSIDE 1st BZ BY SUITABLE CHOICE OF $\vec{G}$

$$E_{0k} = \frac{\hbar^2 k^2}{2m}$$

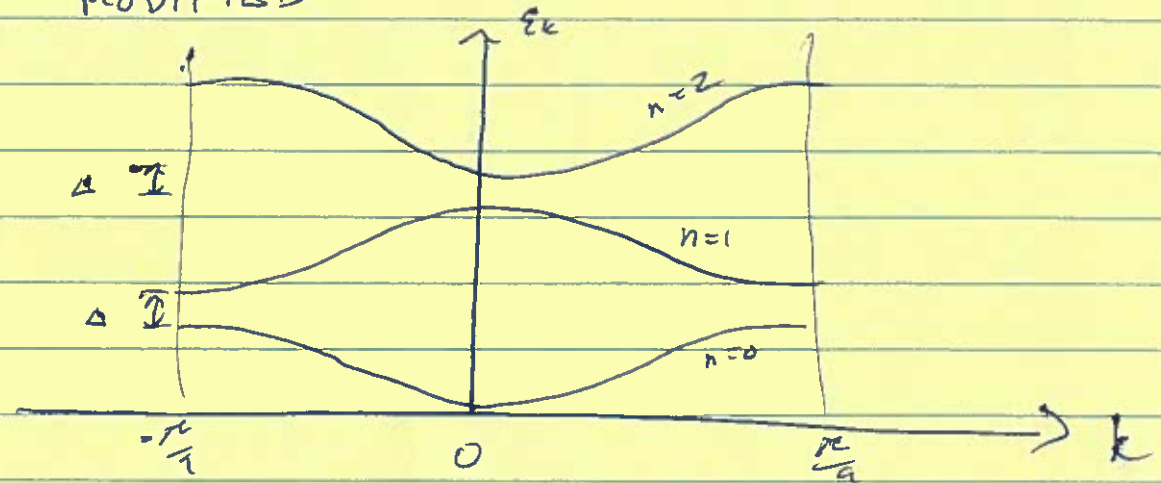
$$E_{1k} = \frac{\hbar^2}{2m} (k - \sin(k) G_1)^2$$

$\vdots$

$$E_{nk} = \frac{\hbar^2}{2m} (k - \sin(k) n G_1)^2$$



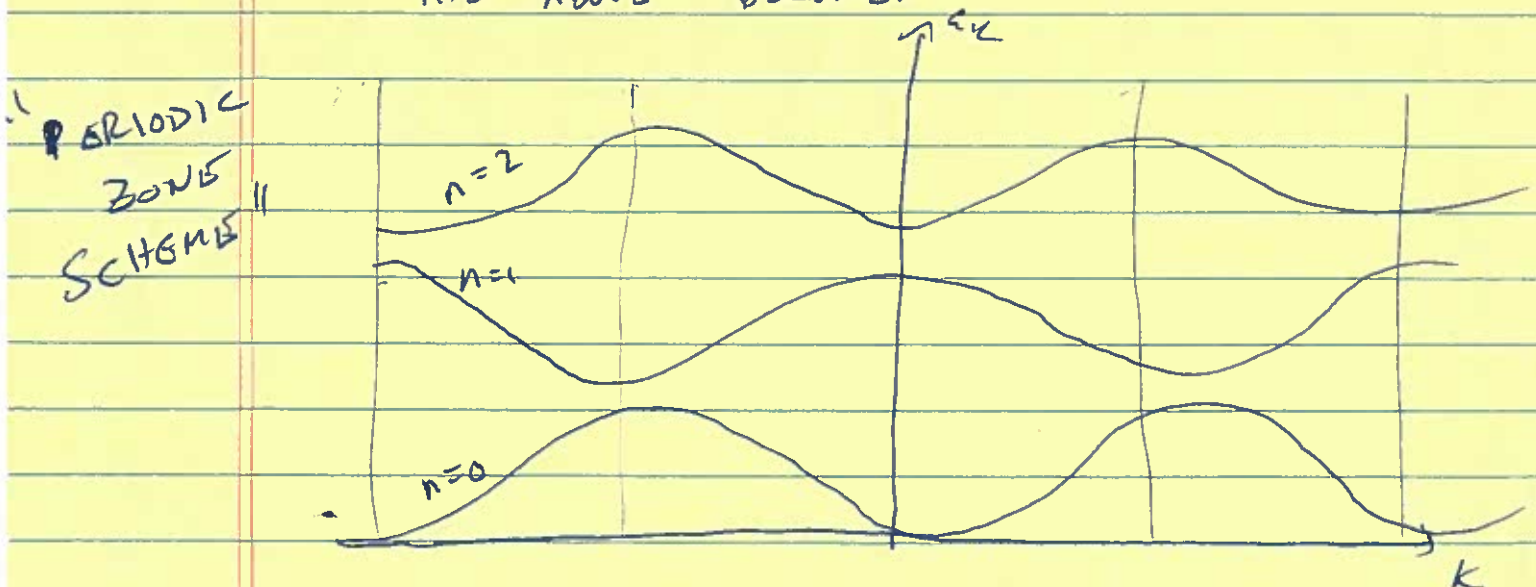
IF WE INCLUDE EFFECTS OF LATTICE AS A PERTURBATION (NEARLY FREE) ELECTRONS, WE HAVE ALREADY SEEN HOW THIS PICTURE GETS MODIFIED



LASTLY, IT IS VERY COMMON TO SIMPLY REPEAT THE FIRST ZONE THROUGH ALL RECIPROCAL SPACE AND ADOPT THE CONVENTION THAT

$$E_{k+G} \equiv E_k$$

IS JUST THE ENERGY OF THE MODE IN THE 1st BZ THE ABOVE BECOMES



EVEN WITH BLOCH'S THM, THE GENERAL SOLUTION TO THE PROBLEM OF AN ELECTRON IN A PERIODIC POTENTIAL IS HARD. THERE ARE SOME SIMPLE EXAMPLES WE CAN DO THOUGH.

WE ALREADY CONSIDERED THE "NEARLY FREE" ELECTRON LIMIT. NOW LET US CONSIDER THE OTHER EXTREME

THE TIGHT BINDING MODEL (NOT "NEARLY BOUND")

THIS IS THE N-ELECTRON VERSION OF THE COVALENT BOND PROBLEM WE CONSIDERED IN LECTURE 3

CONSIDER THE CASE OF AN ELECTRON WITH HAMILTONIAN

$$H = K + \sum_j V_j$$

WHERE

$$K \equiv \frac{p^2}{2m}$$

AND

$$V_j \equiv V(\vec{r} - \vec{R}_j) = \frac{e^2}{|\vec{r} - \vec{R}_j|}$$

BRAGG'S
LATTICE
POSITION

NOW IF $|\phi_j\rangle$ IS THE ATOMIC WAVEFUNCTION OF THE ELECTRON ON SITE $\vec{R}_j$

$$(K + V_j)|\phi_j\rangle = \epsilon_{\text{atomic}}|\phi_j\rangle$$

THEN IT TURNS OUT THE CORRECT SOLUTION FOR THE FULL HAMILTONIAN HAS FORM

$$\begin{aligned} |\psi_{\vec{k}}\rangle &= \sum_{\vec{r}_j} C_{\vec{k}} |\phi_j\rangle \\ &= \sum_j e^{i\vec{k}\cdot\vec{r}_j} |\phi_j\rangle \end{aligned}$$

ONE CAN PROVE THAT THIS ANSATZ SOLUTION HAS BLOCH FORM

$$\begin{aligned} |\psi_{\vec{k}}(\vec{r}+\vec{R})\rangle &= \sum_j e^{i\vec{k}\cdot\vec{r}_j} |\phi_j(\vec{r}+\vec{R}-\vec{r}_j)\rangle \\ &= e^{i\vec{k}\cdot\vec{R}} \sum_j e^{i\vec{k}\cdot(\vec{r}_j-\vec{R})} |\phi_j(\vec{r}-\vec{r}_j+\vec{R})\rangle \\ &= e^{i\vec{k}\cdot\vec{R}} |\psi_{\vec{k}}(\vec{r})\rangle \end{aligned}$$

SINCE WE ARE SUMMING OVER ALL SITES $\vec{r}_j$

QED

NOW, AS WITH THE COVALENT BOND CALCULATION, WE NEED TO DIAGONALIZE THE HAMILTONIAN

$$\begin{aligned} H_{nm} &= \langle \phi_n | \mathcal{H} | \phi_m \rangle \\ &= \langle \phi_n | (K + \sum_j V_j) | \phi_m \rangle \\ &= \epsilon_{\text{ATOMIC}} \delta_{nm} + \sum_{j \neq n} \langle \phi_n | V_j | \phi_m \rangle \end{aligned}$$

RECALL FROM THE COVALENT BOND CALCULATION THAT $\langle \phi_n | V_j | \phi_m \rangle$ ARE OVERLAP INTEGRALS AND PHYSICALLY MANIFESTED AS AN ELECTRON HOPPING FROM SITE $\vec{R}_m$ TO SITE $\vec{R}_n$. THUS IT IS REASONABLE TO SET THIS INTEGRAL TO ZERO (TO A FIRST APPROXIMATION) UNLESS $\vec{R}_m$ AND $\vec{R}_n$ ARE NEAR NEIGHBORS

1D CHAIN EXAMPLE

$$\Rightarrow \langle \phi_n | V_j | \phi_m \rangle = \begin{cases} V_0 & \text{IF } n=m \\ -t & \text{IF } n=m\pm 1 \\ 0 & \text{OTHERWISE} \end{cases}$$

$$H_{nm} = \epsilon_0 \delta_{nm} - t (\delta_{n+1,m} + \delta_{n-1,m})$$

$$\text{WHERE } \epsilon_0 \equiv \epsilon_{\text{atom.c}} + V_0$$

$$\langle \psi_k | H_{\text{tot}} | \psi_k \rangle = \left(\sum_n e^{-i\vec{k} \cdot \vec{r}_n} \langle \phi_n | \right) H \left(\sum_m e^{i\vec{k} \cdot \vec{r}_m} | \phi_m \rangle \right)$$

$$= \sum_{n,m} e^{i\vec{k} \cdot (\vec{r}_m - \vec{r}_n)} \langle \phi_n | H | \phi_m \rangle$$

$$= \sum_n (\epsilon_0 - t(e^{i\vec{k} \cdot \vec{a}} + e^{-i\vec{k} \cdot \vec{a}}))$$

$$= N (\epsilon_0 - 2t \cos(ka))$$

$$\epsilon_k = \epsilon_0 - 2t \cos(ka)$$

OR IF STAYED IN 3D, ON A SIMPLE CUBIC LATTICE FOR EXAMPLE, WE WOULD HAVE HAD A COSINE FOR EVERY PAIR OF NEAREST NEIGHBORS

$$\epsilon_c = \epsilon_0 - 2t(\cos k_x a + \cos k_y a + \cos k_z a)$$

IN ALL CASES, AND ~~Q~~ QUITE GENERALLY, FOR $ka \ll 1$

$$\epsilon_c = \epsilon_0^* - \frac{t^2}{2} k_a^2$$

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

$\Rightarrow$ PARABOLIC BANDS WITH EFFECTIVE MASS $m^* = \frac{\hbar^2}{2ta^2}$

