PHYS 460 LECTURE 11

WE ENDED LAST LECTURE TALKING ABOUT THE TIGHT-BINDING MODEL, BUT THINGS WERE A LITTLE RUSHED. SO, LET'S BEGIN TODAY WITH A QUICK REVIEW, WHICH WILL ALLOW US TO TALK ABOUT SOME SALIENT FEATURES OF THE RESULT.

LET'S RESTRICT OUR ATTENTION TO THE 1D CHAIN FOR NOW. IN THIS CASE

$$\mathcal{H} = K + \sum_n V_n \quad \text{WHERE } V_n \equiv \frac{-e^2}{(x-na)^2}$$

WE CHOSE AN ANSATZ SOLUTION OF THE FORM

$$|\psi_k\rangle = \sum_n e^{ikna} |\phi_n\rangle$$

$$\text{WHERE} \quad V_n |\phi_n\rangle = \varepsilon_{atomic} |\phi_n\rangle$$

AND IN FACT, I SHOWED THAT THIS SOLUTION WAS OF BLOCH FORM.

ASSUMING ONLY INTERACTIONS BETWEEN NEAREST NEIGHBORS, WE ALSO SAW

$$H_{nm} \equiv \langle \phi_n | \mathcal{H} | \phi_m \rangle$$

$$= \langle \phi_n | \left(K + \sum_j V_j \right) | \phi_m \rangle$$

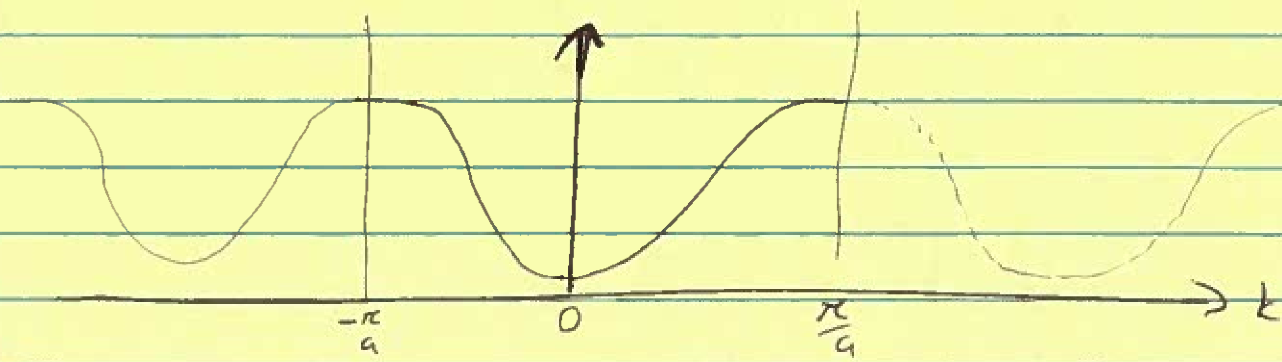
$$= \underbrace{(\varepsilon_{atomic} + V_0)}_{\varepsilon_0} \delta_{nm} - t \left(\delta_{n+1,m} + \delta_{n-1,m} \right)$$

$$\Rightarrow \varepsilon_{\vec{k}} = \frac{\langle \psi_{\vec{k}} | H | \psi_{\vec{k}} \rangle}{N} = \frac{1}{N}\left(\sum_n e^{-ikna} \langle \phi_n |\right) H \left(\sum_m | \phi_m \rangle e^{ikma}\right)$$

$$= \frac{1}{N} \sum_{n,m} e^{ik(m-n)a} \left(\varepsilon_0 \delta_{nm} - t\,\delta_{n+1,m} - t\,\delta_{n-1,m}\right)$$

$$= \varepsilon_0 - t e^{ika} - t e^{-ika}$$

$$= \varepsilon_0 - 2t \cos(ka)$$



MORE GENERALLY, ONE CAN SHOW THAT IN 3D, THE BAND WILL BE DESCRIBED BY DISPERSION

$$\varepsilon_{\vec{k}} = \varepsilon_0 - t \sum_{\{\vec{m}\}} e^{i\vec{k}\cdot\vec{m}}$$

WHERE $\{\vec{m}\}$ ARE THE SET OF ALL NEAREST NEIGHBOUR VECTORS

FOR SIMPLE CUBIC, FOR EXAMPLE

$$\varepsilon_{\vec{k}} = \varepsilon_0 - 2t\left[\cos k_x a + \cos k_y a + \cos k_z a\right]$$

THERE ARE SEVERAL INTERESTING THINGS TO NOTE HERE

(1) AS NOTED EARLIER, IN THE LIMIT $ka \ll 1$

$$\varepsilon_k \approx \varepsilon_0 + t k^2 a^2$$

WHICH IS SORT OF LIKE $\varepsilon_{k,\text{free}} = \frac{1}{2}\frac{\hbar^2 k^2}{m}$

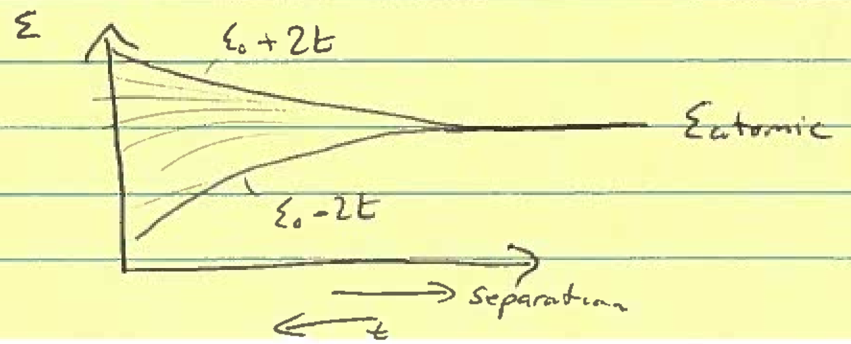
$\Rightarrow$ EVEN IN THE TIGHTLY BOUND LIMIT, ELECTRONS LOOK LIKE FREE PARTICLES FOR SMALL ENOUGH k. THE EFFECTIVE MASS, m^*, IS

$$m^* = \frac{\hbar^2}{2ta^2}$$

THIS IS A GENERAL RESULT

(2) THE ENERGY OF ELECTRONS IN THIS BAND ARE BOUND BY THE LIMIT $\varepsilon_0 - 2t < \varepsilon_k < \varepsilon_0 + 2t$

THE QUANTITY $\Delta\varepsilon_k = 2t$ IS KNOWN AS THE "BAND WIDTH" AND GETS LARGER FOR GREATER INTERACTION. THIS AGAIN IS A GENERAL RESULT



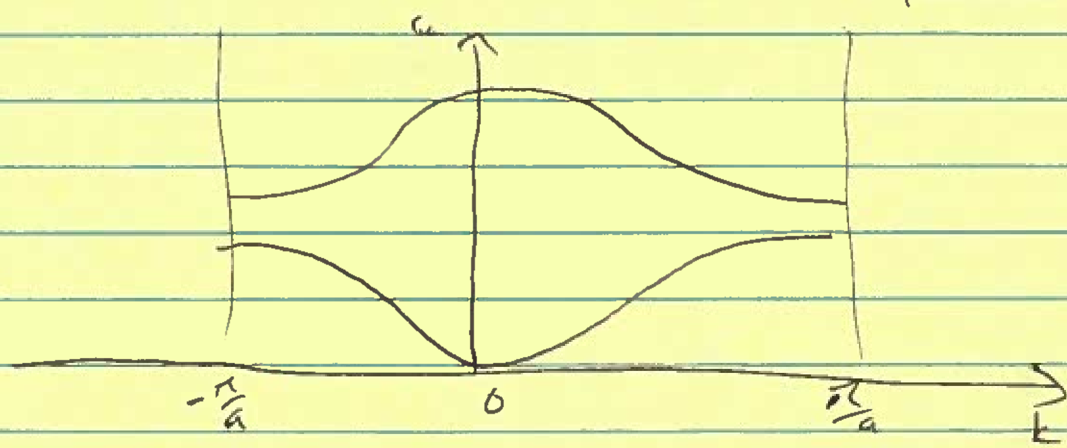
(3) FOR BANDS THAT ARE LESS THAN OR EQUAL TO HALF FULL, TOTAL ENERGY IS <u>DECREASED</u> BY THE FORMATION OF THE BAND,

→ THIS IS THE ORIGIN OF METALLIC BONDING!

THERE ARE SEVERAL NATURAL EXTENSIONS TO THE TIGHT-BINDING MODEL. 3D CRYSTAL STRUCTURES, OF COURSE, BUT ALSO

(I) MULTIPLE ATOMS PER UNIT CELL, TYPE A (ENERGY ε_A) AND B (ENERGY ε_B) WITH HOPPING t BETWEEN

ANALYSIS IS STRAIGHTFORWARD, BUT END RESULT IS THE FORMATION OF HIGHER AND LOWER BANDS. (WE DON'T SAY ACOUSTIC/OPTICAL FOR ELECTRONS)

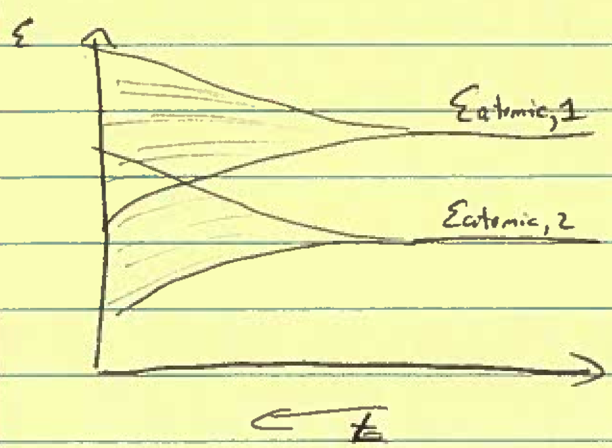


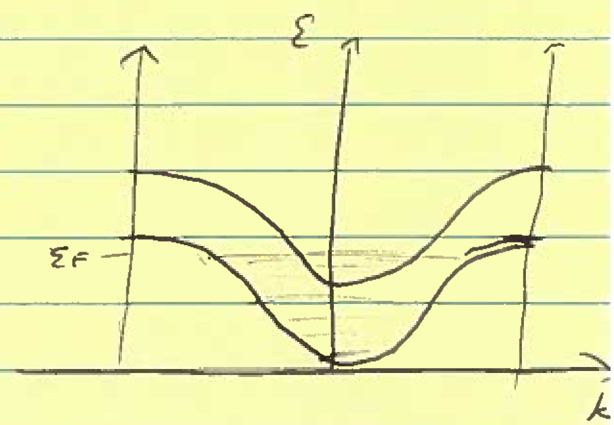
NOTE THIS LOOKS LIKE DIATOMIC CHAIN PHONON DISPERSION, WITH QUADRATIC RATHER THAN LINEAR LOW k DISPERSION

II EACH ATOM IN THE CHAIN (OR UNIT CELL) CAN CONTRIBUTE MORE THAN ONE TYPE OF ORBITAL (e.g. 2s, 2p, 3s, 3p, 3d....)

AGAIN, GENERALIZING OUR PREVIOUS RESULT IS A SIMPLE MATTER, BUT THE END RESULT IS THAT WE GET A NEW BAND PER ORBITAL

THESE BANDS CAN OVERLAP, WHICH HAS CONSEQUENCES



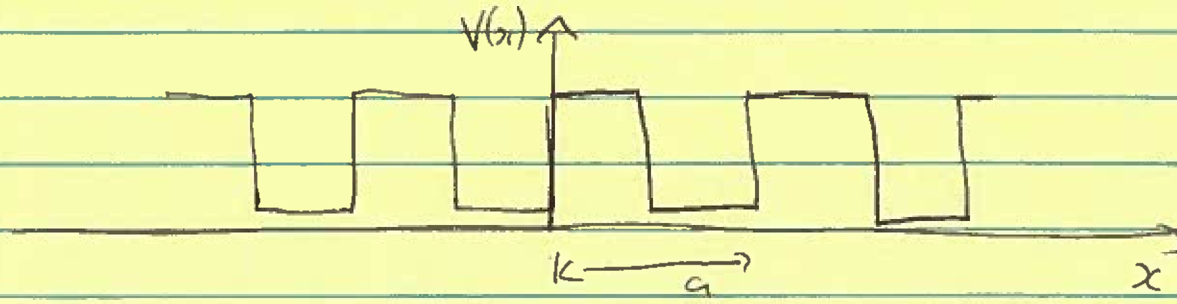


IN PRACTICE, TIGHT BINDING CALCULATION ARE FREQUENTLY USED TO DESCRIBE BANDS ORIGINATING FROM CORE ELECTRONS OR ORBITALS WITH DENSITY CLOSE TO THE NUCLEUS.

NOTE THAT IF WE INCLUDED ALL POSSIBLE ORBITALS FOR ALL ATOMS IN OUR CALCULATION, THE TIGHT-BINDING MODEL WOULD EVOLVE SMOOTHLY TO THE FREE ELECTRON MODEL WITH INCREASING t

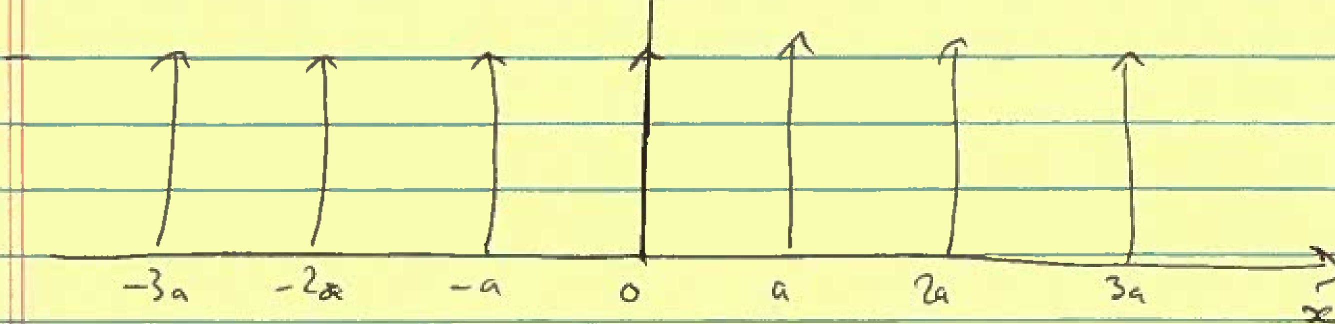
WE NOW SEEN BANDS IN WEAK AND STRONG INTERACTION LIMITS. IT IS WORTHWHILE TO CONFIRM THE EXISTENCE OF BANDS FOR SOMETHING IN THE MIDDLE. FOR THIS PURPOSE, WE CAN LOOK AT ANOTHER COMMON "TOY MODEL" IN 1D: <u>THE KRONIG-PENNEY MODEL</u> (SIMON, PROBLEM 15.6)

THE KRONIG-PENNEY MODEL IS A GOOD OLD FASHIONED SCHRODINGER WAVE PROBLEM IN A PERIODIC SQUARE WELL



IT IS SOLUABLE, BUT MESSY, SO WE WILL INSTEAD CONSIDER A SPECIAL LIMITING CASE, WHERE THE BARRIER POTENTIALS CAN BE APPROXIMATED BY DIRAC DELTA FUNCTIONS

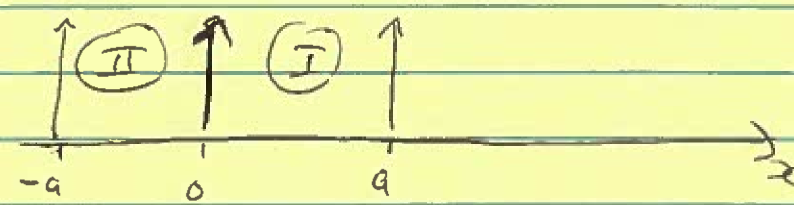
$$V(x) = a\mathcal{U}\sum_n \delta(x - na)$$



THE FULL SCHRODINGER EQUATION IS THEN

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \alpha\sum_n \delta(x-na)\psi = E\psi$$

WE CAN SOLVE THIS BY FIRST CONSIDERING THE WAVE IN BETWEEN THE DIRAC DELTA FUNCTIONS. IN PARTICULAR, DEFINING ZONES I & II AS SUCH



IN THESE ZONES $V(x)=0$

$$\Rightarrow \psi_{I} = Ae^{iqx} + Be^{-iqx}$$

AND $\psi_{II} = Ce^{iqx} + De^{-iqx}$

WHERE $q = \frac{\sqrt{2mE}}{\hbar}$

WE WILL APPLY BOUNDARY CONDITIONS, BUT FIRST, WE CAN USE BLOCH'S THEOREM

$$\psi(x) = e^{ika}\psi(x-a)$$

OR FOR US $\psi_{II}(x) = e^{ika}\psi_{I}(x-a)$

THIS CAN ONLY BE TRUE FOR ALL x, q IF THE COEFFICIENTS OF e^{iqx} AND e^{-iqx} ARE INDEPENDENTLY EQUAL

$$\Rightarrow \quad C = A e^{ika} e^{-iqa}$$

$$\text{AND} \quad D = B e^{ika} e^{iqa}$$

$$\Rightarrow \psi_{II}(x) = e^{ika}\left[A e^{iq(x-a)} + B e^{-iq(x-a)}\right]$$

NOW WE APPLY BOUNDARY CONDITIONS, WHICH ARE TRICKY DUE TO THE PRESENCE OF THE DELTA FUNCTIONS. IT TURNS OUT ψ IS STILL CONTINUOUS AT $x=0$

$$\therefore \quad \psi_{I}(0) = \psi_{II}(0)$$

$$\boxed{A + B = e^{ika}\left[A e^{-iqa} + B e^{iqa}\right]} \quad (\#)$$

ψ IS NOT SMOOTH AT $x=0$, BUT WE FIND THE SIZE OF THE DISCONTINUITY IN $\frac{d\psi}{dx}$ BY INTEGRATING THE SCHRODINGER EQUATION OVER THE RANGE $-\varepsilon < x < \varepsilon$

$$-\frac{\hbar^2}{2m}\int_{-\varepsilon}^{\varepsilon} \frac{d^2\psi}{dx^2}\,dx + a\mathcal{U}_0 \int_{-\varepsilon}^{\varepsilon} \delta(x)\psi(x)\,dx = E\int_{-\varepsilon}^{\varepsilon} \psi(x)\,dx$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{d\psi_{II}}{dx}(x=0) - \frac{d\psi_{I}}{dx}(x=0)\right) + \mathcal{U}_0\,\psi_{I}(x=0) = 0$$

$$-\frac{\hbar^2}{2m}\left(iqAe^{i(ka-qa)} - iqBe^{i(ka+qa)} - iqA + iqB\right) + U_0(A+B) = 0$$

$$\Rightarrow \boxed{Ae^{i(ka-qa)} - Be^{i(ka+qa)} - A + B - \frac{2mU_0}{i\hbar^2 q}(A+B) = 0} \quad (**)$$

OR EXPRESSING (*) & (**) IN SUCH A WAY THAT GROUPS COEFFICENTS OF A & B

$$(*) \longrightarrow A\big(\overbrace{1 - e^{ika - iqa}}^{C_1}\big) + B\big(\overbrace{1 - e^{ika+iqa}}^{C_2}\big) = 0$$

$$(**) \longrightarrow A\Big(\underbrace{e^{i(ka-qa)} - 1 - \frac{2mU_0}{i\hbar^2 q}}_{C_3}\Big) + B\Big(\underbrace{-e^{i(ka+qa)} + 1 - \frac{2mU_0}{i\hbar^2 q}}_{C_4}\Big) = 0$$

2 COUPLED LINEAR EQUATIONS

$$\begin{pmatrix} C_1 & C_2 \\ C_3 & C_4 \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix} = 0$$

$\alpha = \frac{2mU_0}{i\hbar^2 q}$

SOLUTION IFF $C_1C_4 - C_2C_3 = 0$

$$\left(1 - e^{i(ka-qa)}\right)\left(-e^{i(ka+qa)} + 1 - \alpha\right) - \left(1 - e^{i(ka+qa)}\right)\left(e^{i(ka-qa)} - 1 - \alpha\right) = 0$$

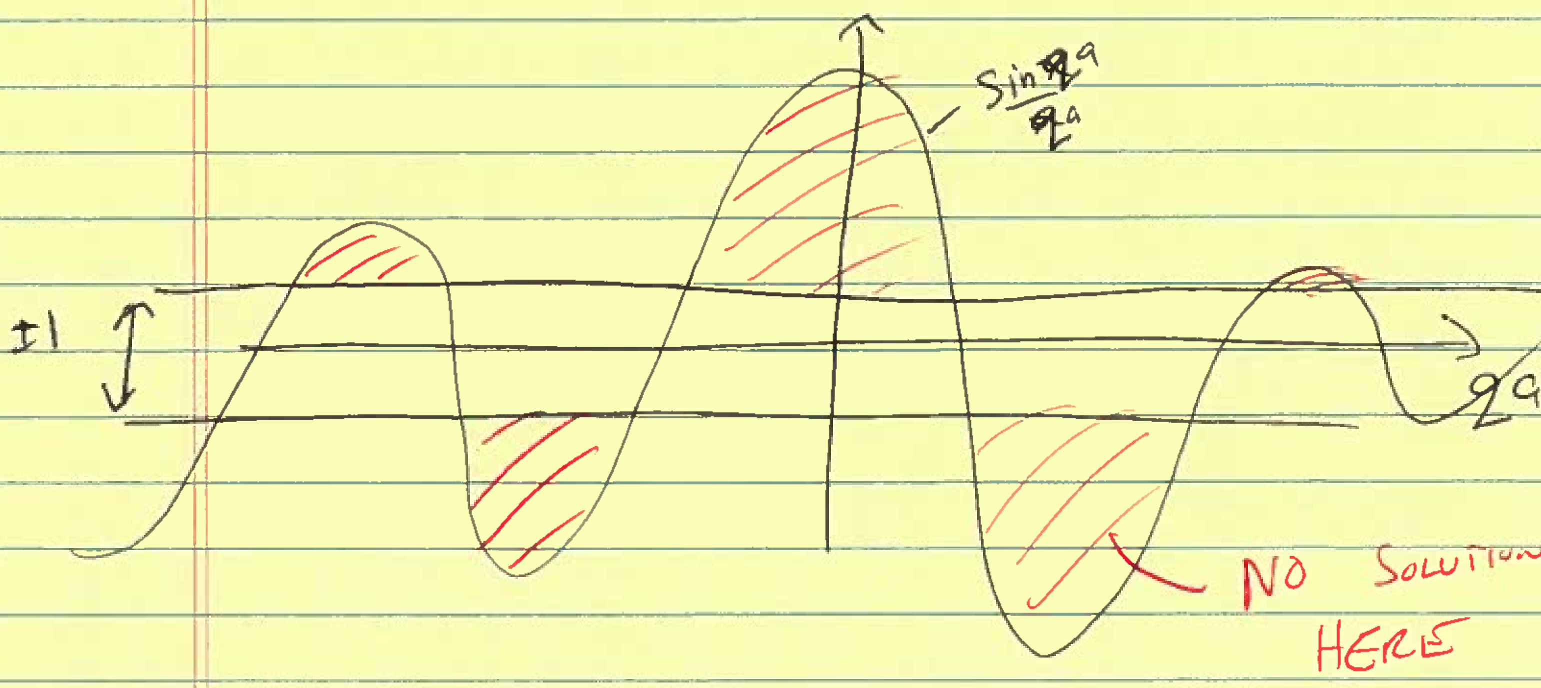
WHICH REDUCES TO

$$\boxed{\cos ka = \cos qa + \frac{mU_0}{\hbar^2 q}\sin qa}$$

THIS IS A TRANSCENDTAL EQUATION WITHOUT A GENERAL SOLUTION. YOU CAN SEE THOUGH THAT NOT ALL VALUES OF q (AND THUS E) ARE ALLOWED.

THE LHS OF THE EQUATION IS BOUNDED IN THE REGION $-1 \leq \cos ka \leq 1$, WHILE FOR $qa \to 0$, THE RHS $= 1 + \frac{m u_0 a}{\hbar^2} > 1$

MORE GENERAL, WE CAN PLOT THE TWO SIDES AND LOOK FOR INTERSECTIONS



$\Rightarrow$ SOME q HAVE NO SOLUTION AND THUS SOME $E = \frac{\hbar^2 q^2}{2m}$ AS DISALLOWED!

WE CAN PUSH THIS MODEL TO ANY LIMIT TO CONNECT WITH PREVIOUS MODELS. SIMON SUGGESTS A CONNECTION WITH NEARLY FREE ELECTRONS.

HERE, I AM GOING TO INSTEAD EXPLORE THE LARGE U_0 LIMIT.

IN THIS LIMIT, THE SECOND TERM ON THE RHS IS DOMINANT, AND SOLUTIONS ARE VERY CLOSE TO ZEROS OF $\frac{\sin x}{x}$. THE FIRST ZERO IS $x = \pi$, SO LET'S EXPAND ABOUT THIS

$$qa \approx \pi - \delta \quad \leftarrow \text{SMALL REAL NUMBER}$$

$$\Rightarrow \quad \cos ka \approx -1 + \delta^2 + \frac{mU_0 a}{\hbar^2} \left(\frac{\delta}{(\pi - \delta)} \right)$$

$$= -1 + \delta^2 + \frac{mU_0 a}{\hbar^2} \frac{\delta}{\pi} \left(1 + \frac{\delta}{\pi} \right)$$

$$\approx -1 + \frac{mU_0 a}{\hbar^2} \frac{\delta}{\pi}$$

$$\delta = \frac{\pi \hbar^2}{mU_0 a} (1 + \cos ka)$$

$$\frac{\sqrt{2mE}\, a}{\hbar} = qa = \pi - \frac{\pi \hbar^2}{mU_0 a} (1 + \cos ka)$$

$$E = \frac{\hbar^2}{2m} \left(\frac{\pi}{a^2} - \frac{\pi \hbar^2}{mU_0 a^2} (1 + \cos ka) \right)$$

$$= E_0 - 2t (1 + \cos ka)$$

or $$E_k = E_0 - 2t - 2t\cos ka$$
$$= E_0' - 2t\cos ka$$

THE TIGHT BINDING SOLUTION!

NEXT: PREDICTING WHEN SOMETHING IS A METAL & MEASURING BAND STRUCTURE