Nearly - free electrons

Suppose the lattice potential is weak — eigenstates should be constructed from plane waves.

(1) General method

$$H\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + U\right]\psi = E\psi.$$

$$U(\underline{r}+\underline{R}) = U(\underline{r}) \Rightarrow \underbrace{U(\underline{r}) = \sum_{\underline{G}} U_{\underline{G}} e^{i\underline{G}.\underline{r}}}_{\text{Fourier series.}} \qquad \boxed{\underline{G}.\underline{R} = 2\pi n.}$$

Expand $\psi(\underline{r}) = \sum_{\underline{k}} c_{\underline{k}} e^{i\underline{k}.\underline{r}}$ — all $\underline{k}$ for the moment.

$$\sum_{\underline{k}} \left[\left(\frac{\hbar^2 k^2}{2m} - E\right) c_{\underline{k}} e^{i\underline{k}.\underline{r}} + \underbrace{\sum_{\underline{G}} c_{\underline{k}} U_{\underline{G}} e^{i(\underline{k}+\underline{G}).\underline{r}}}_{\substack{\text{rewrite } \underline{k}' = \underline{k}+\underline{G} \\ c_{\underline{k}'-\underline{G}} U_{\underline{G}} e^{i\underline{k}'.\underline{r}} \\ \text{but } \underline{k}' \text{ dummy variable}}}\right] = 0$$

$$\Rightarrow \sum_{\underline{k}} \underbrace{\left[\left(\frac{\hbar^2}{2m} k^2 - E\right) c_{\underline{k}} + \sum_{\underline{G}} c_{\underline{k}-\underline{G}} U_{\underline{G}}\right]}_{\text{must vanish for every } \underline{k}.} e^{i\underline{k}.\underline{r}} = 0$$

N.B. — not all $\underline{k}$ are mixed $\Rightarrow$ only $\underline{k}$, $\underline{k}-\underline{G}$, $\underline{k}-2\underline{G}$ .... etc.

Thus $\psi_{\underline{k}}(\underline{r}) = \sum_{\underline{G}} c_{\underline{k}-\underline{G}} e^{i(\underline{k}-\underline{G}).\underline{r}} = e^{i\underline{k}.\underline{r}} u_{\underline{k}}(\underline{r})$

$\downarrow$ periodicity of lattice $\rightarrow$ Bloch th^{m}

1D chain (again).

Not atoms but a fn^1

$$U(x) = \frac{1}{2} U_0 \cos \frac{2\pi x}{a} \quad \text{— latt. const}$$

Recip lattice $G = \frac{2\pi}{a}.n.$

$U_0 C_{k-\frac{4\pi}{a}} \qquad \left(k+\frac{2\pi}{a}\right)^2 - E \; C_{k+\frac{2\pi}{a}} \qquad U_0 C_k$

$U_0 C_{k+\frac{2\pi}{a}} + (k^2 - E) C_k + U_0 C_{k-\frac{2\pi}{a}}$

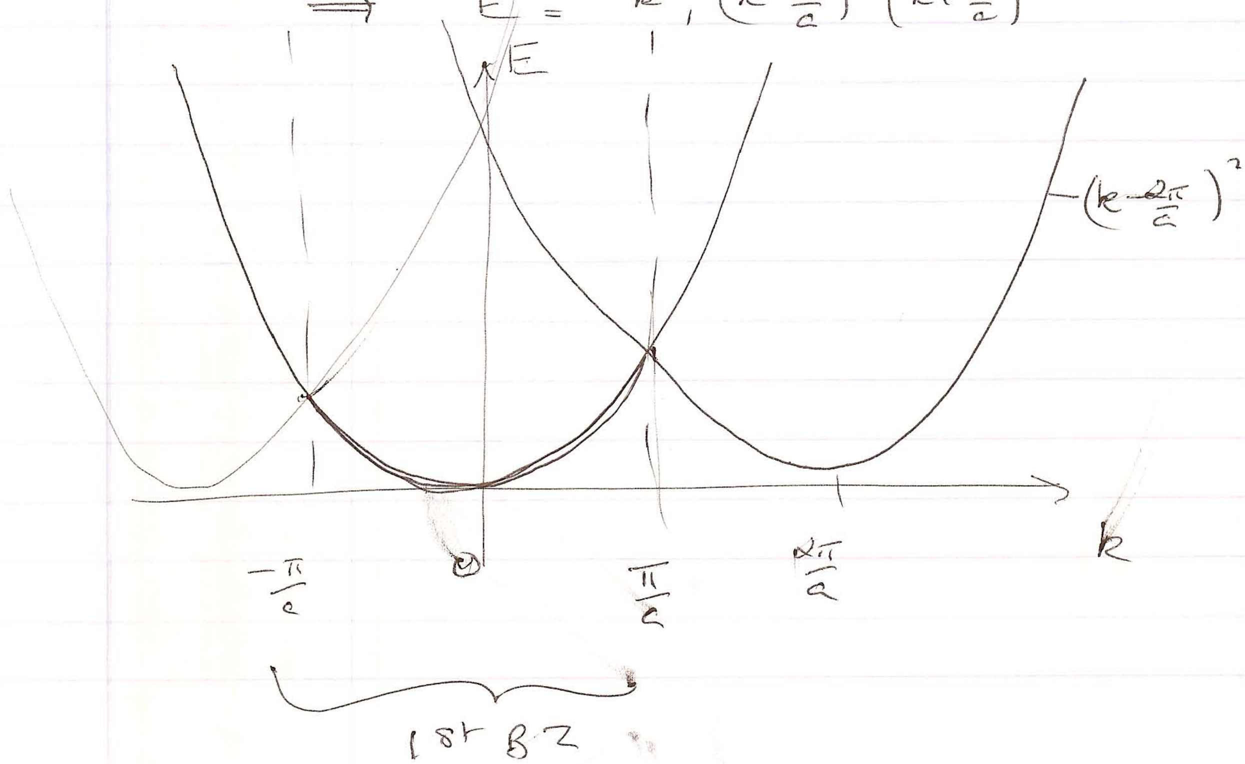
$U_0 \qquad \left(k-\frac{2\pi}{a}\right)^2 - E \; C_{k-\frac{2\pi}{a}} \qquad U_0$

U_0

Suppose U_0 small. (

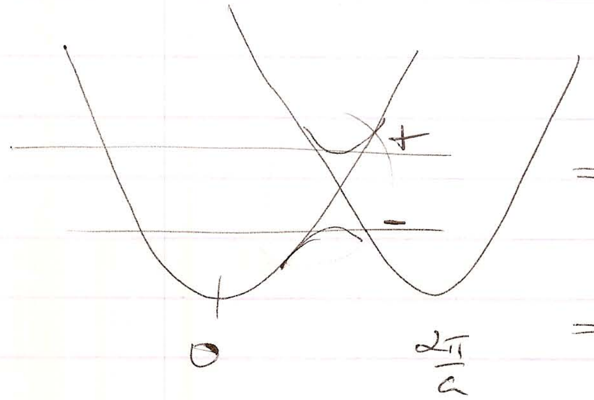
(a) $U_0 = 0$

$\Rightarrow E = k^2, \left(k-\frac{2\pi}{a}\right)^2 \left(k+\frac{2\pi}{a}\right)^2$



(b) Now turn on U_0, but very small.

— no difference except near <u>degeneracies</u>



$$\Rightarrow \begin{vmatrix} k^2 - E & U_0 \\ U_0 & \left(k - \frac{2\pi}{a}\right)^2 - E \end{vmatrix} = 0$$

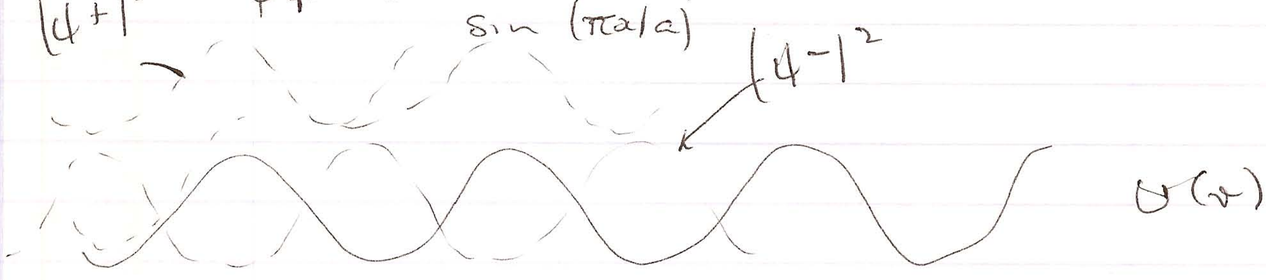
$\Rightarrow$ when $k = \frac{\pi}{a}$, degenerate

Sol$^{\underline{n}}$

$$E = \frac{1}{2}\left[k^2 + \left(k - \frac{2\pi}{a}\right)^2\right] \pm \frac{1}{2}\sqrt{\left[\left(k^2 - \left(k - \frac{2\pi}{a}\right)^2\right)^2 + 4|U_0|^2\right]}$$

at $k = \frac{\pi}{a}$ $\Rightarrow$ $\frac{\pi^2}{a^2} \pm |U_0|$

$\psi^{\mp} = \begin{matrix} \cos(\pi x/a) \\ \sin(\pi x/a) \end{matrix}$



o Standing waves — in phase with potential

$$e^{ik.r} \longleftrightarrow \pm e^{i\left(k - \frac{2\pi}{a}\right).r} \quad \text{at } k = \pi/a$$

o Band gap results from "coherent backscattering" on zone-boundary.

o Criterion is $k = \frac{1}{2}G$

$\left(\text{or } \underline{k}.\underline{G} = \left|\frac{1}{2}\underline{G}\right|^2\right) \Rightarrow$ just Bragg scattering in xtal.

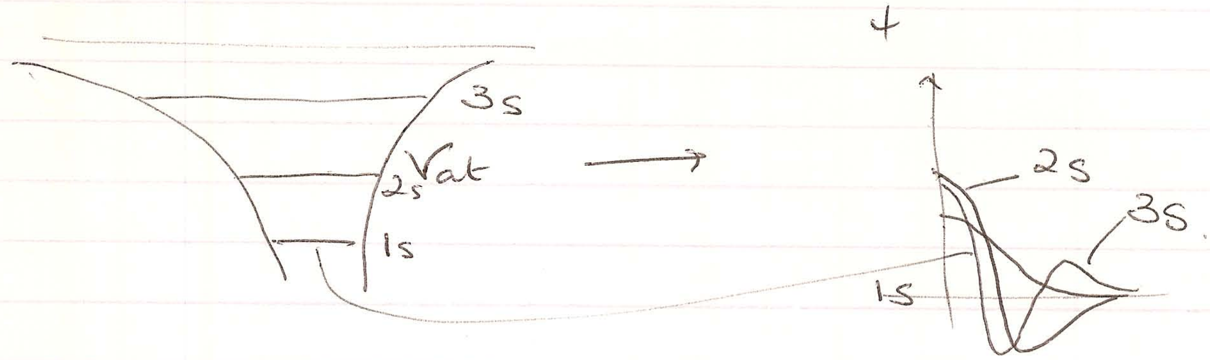
Pseudopotential

plane waves a sensible approx if

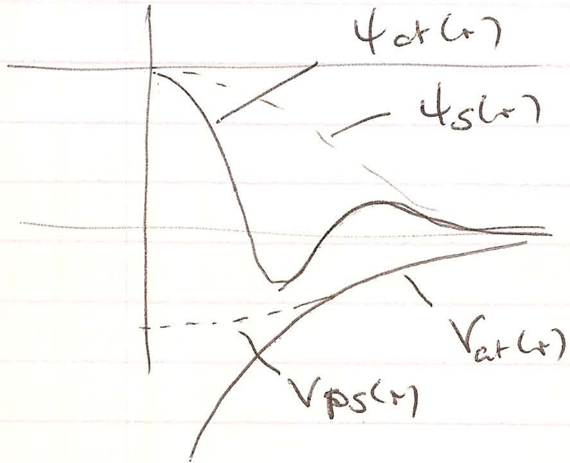
U_Q small (ie $U \ll KE$.)

But real potential $= \dfrac{Ze^2}{r} \sim \dfrac{Ze^2}{a_B} \rightarrow$ large

Idea: Interested in valence bands, not states in core



$\rightarrow$ Construct a potential that has the same eigenvalues as 3s, but without 1s, 2s... & core states



V_{ps} can be weak

$\rightarrow$ Other routes — have the same scattering cross section at low E