Solids (Gr-218)

1) Griffiths does the free electron gas model (first worked out by Arnold Sommerfeld (1868–1951) in ~1927 when QM was just born — proving that old dogs can learn new tricks)

It's only quasi-free since confined by a broad flat-bottomed potential well.

+ a simple version of Bloch theory (developed originally by Felix Bloch (1905–1983)) which introduces a periodic potential in an unbounded, but finite, space.

We will just do the free electron gas model.

F402

It's enough — and Griffiths leaves too many holes in the explandtion of the Bloch theory for my taste.
(free electron gas model usually thought of for metals but it also applies to all solids to some degree.)

But first ~~as~~ a long overdue digression, ~~we'll~~ on why there are quantized bound states in general.

2) Bound energy eigen States are Quantized

Specific special cases

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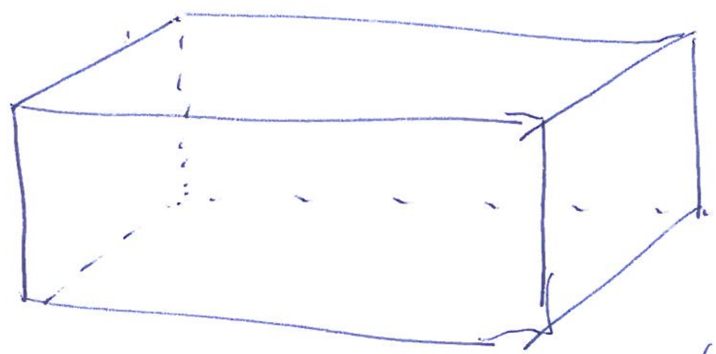
show that bound ~~stale~~ ~~c~~ states with $E < V_\infty$) are quantized.

a) 1-d infinite-square well

b) Multi-d infinite-square well where the well is a right cuboid or rectangular box (Wiki: Cuboid)



which is a simple generalization of the 1-d infinite square well.

c) finite square well in 1-d

d) 1-d Simple harmonic oscillator

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e) Hydrogenic atom.

On the other hand, we know unbound energy eigenstates ($E > V_\infty$) are not quantized for free particles with V = constant everywhere (Gr-59)

We might intuit that bound energy eigenstates ($E < V_\infty$) ~~with~~ are always quantized & unbound energy eigenstates ($E > V_\infty$) are always unquantized. This is true — although

one should keep in mind
that their may be
some pathological cases
where it's not true
(in ideal & maybe real cases)

But is there a general proof..?
I don't know, but probably

Is there a general proof
with in our range?
Probably not or someone
would have given it.

We can however give
a 1-d proof (which
has a few holes in it)
but is reasonably
satisfying from
Cohen-Tannoudji - 352
that bound states are quantized.

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~~Spl $V_0 = 0$, not but~~
~~usually~~

a) First let's consider 1-d
time-independent Sch. equ.

$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi$$

rewrite to

~~$$\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}$$~~

$$\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}(V - E)\psi$$

Define $\kappa = \sqrt{\frac{2m}{\hbar^2}(V - E)}$

if $V - E < 0$ or $E > V$

define $k = \sqrt{\frac{2m}{\hbar^2}(E - V)}$ where $\kappa = ik$

$$\therefore \quad \frac{\partial^2 \psi}{\partial x^2} = k^2 \psi$$

In general k is a function of position since $V = V(x)$ in general.

But if V varies sufficiently slowly over some range, then we can approximate it as a constant over that range.

Then we get general solution for E.

$$\psi = Ae^{kx} + Be^{-kx} \quad \text{and} \quad \psi = Ae^{+ik_x x} + Be^{-ik_x x}$$

$$E < V \qquad\qquad E > V$$

— There is a degeneracy of 2, in fact for a given E.

Also for $E = V$,

$$\psi = A + Bx$$

which is a knife-edge solution. As an ideal limit, it is an interesting/annoying case, but in practical problems probably is almost always unimportant. (So we only worry about it for obsessive-compulsive reasons).

So essentially, we have exponential or oscillatory solutions at least over small ranges

Isolated Points where $E \simeq V$, are

are tricky.

Mentally in this proof we just interpolate over them.

Note growing to infinity exponential solutions can't be normalized and have to be ruled out.

We have this problem. Nature doesn't — such solutions just never develop dynamically in ~~ordinary~~ Sch. eqn. evolution or in wave function collapse

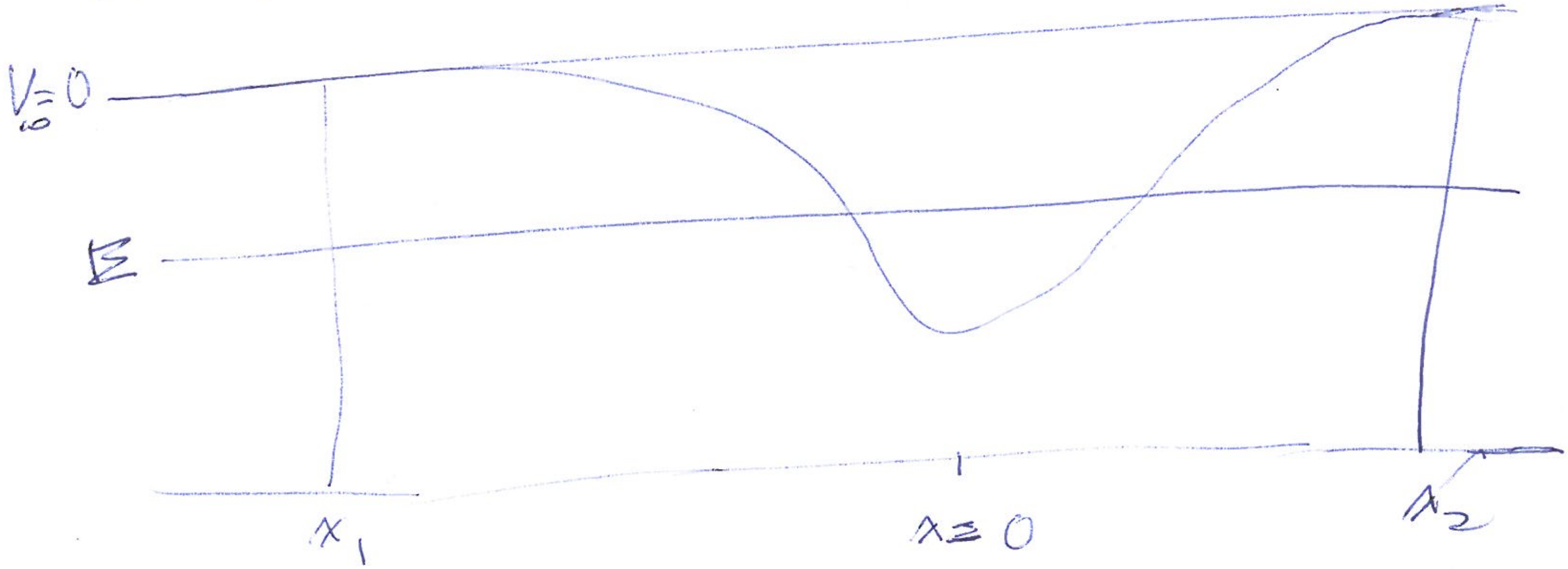
which conserves probability density

likewise.

5-410

Ruling out such solutions mathematically proves quantization.

Set $V_\infty = 0$ as usual, and consider a potential well



Consider energy-eigen state ψ with $E < V_\infty$.

So it is a bound state.

Set x_1 and x_2 so far from the center of the potential that $V = V_\infty$.

~~$V = V_\infty$~~

For some ideal potentials this is NOT possible:

~~e.g.~~ e.g., infinite square well

and ideal SHO

but we already know those have quantized energy eigenstates.

— for real potential wells one can be far enough away that $V = V_\infty$ approximately to any degree one likes — or that the well has lost its~~s~~ identity due to myriad perturbations of particles, fields, other bound systems, etc.

At x_1,

we have $V_\infty - E$ = constant

and so

$$\psi(x) = Ae^{\kappa x}$$

A is the normalization constant. It can be fixed arbitrarily say to A = 1 ~~until~~ for a mathematical study of ψ's overall shape. A is just an overall scale factor.

— the $e^{-\kappa x}$ solution is unnormalizable and so its ruled out.

We now integrate

$$\cancel{\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}}$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}(V - E)\psi$$

by an ideal exact mathematical procedure to x_2

where $V = V_\infty$ a constant again.

at x_2

$$\psi(x) = B_+ e^{\kappa x} + B_- e^{-\kappa x}$$

For the setup given,

$$B_+ = B_+(E)$$

it is a function of E alone.

digression

Note $E > V_{min}$ in QM, except $E = V_{min}$ is possible for ~~the other~~ periodic BC cases or free particle

$$\langle E \rangle = \langle \phi | H | \phi \rangle$$

where $|\phi\rangle$ is any state not necessarily a stationary state.

In both case ψ = Constant for the equality to hold.

$$= \langle \phi | T | \phi \rangle + \langle \phi | V | \phi \rangle$$

$$= \frac{\langle \phi | p\, p | \phi \rangle}{2m} + \langle \phi | V | \phi \rangle$$

$$= \cancel{\frac{\langle \phi | p\, p | \phi \rangle}{2m}}$$

5 - 414

$$= \frac{\langle \phi | p^\dagger p | \phi \rangle}{2m} + \langle \phi | V | \phi \rangle$$

since $p = p^\dagger$
for an observable.

$\langle \phi | p^\dagger p | \phi \rangle$
is the inner product of
a ket with itself
and so $\langle \phi | p^\dagger p | \phi \rangle \geq 0$

When can it be zero

$$p|\phi\rangle = p \int dp' |p'\rangle\langle p'|\phi\rangle$$

Only for $|\phi\rangle = |p' = 0\rangle$
eigenstate of
momentum.
Impossible ~~for~~ a free
particle in infinite space
(because unnormalizable)
but possible with periodic BC.

$\langle x | p' = 0 \rangle$ = Constant.

Recall
$\psi = \frac{e^{ipx/\hbar}}{\sqrt{2\pi}}$
are unnormalizable
eigenstate of
p_{op}
for infinite
space.
$p \in (-\infty, \infty)$
for infinite
space.
ψ = Constant
is allowed.

So

$$\langle E\rangle = \langle\phi|H|\phi\rangle > \langle\phi|V|\phi\rangle$$

$$> \langle\phi|V_{min}|\phi\rangle$$

$\therefore \langle E\rangle > \langle V_{min}\rangle$

(except for $|\phi\rangle = |P' = 0\rangle$ when equality holds.)

$\boxed{\text{If } |\phi\rangle \text{ is an energy eigenstate ~~whic~~ with energy } E, \text{ then } E > \langle V_{min}\rangle}$

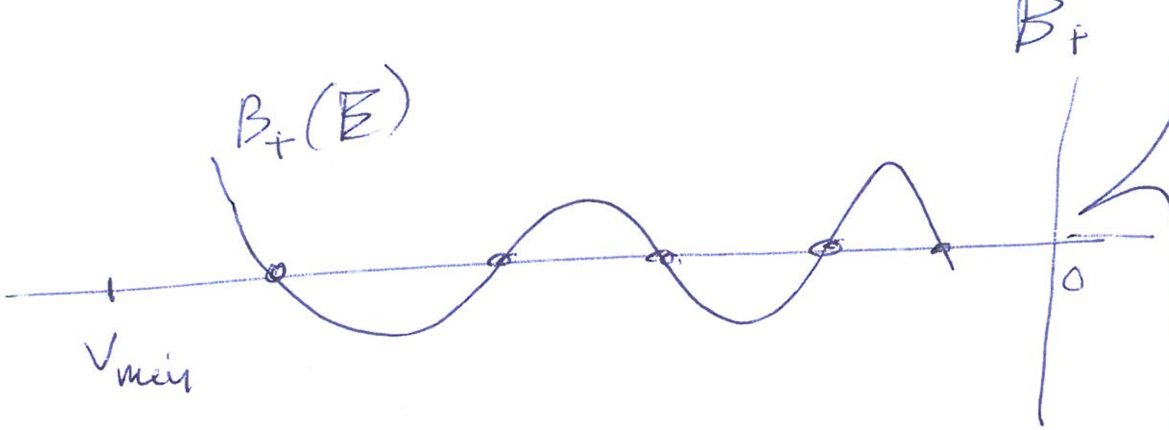
To resume

$$B_+ = B_p(E).$$

But our solution is only normalizable and so physically allowed if

5-416

$$B_+(E) = 0$$



$B_+(0) = ?$ Does it have a general behavior? Don't know.

It is hard to imagine that $B_+(E)$ is zero over any extended region. Perhaps such pathological cases exist, but no one comments on them or has found them. (Not CT-354 anyway)

So only a discrete set of zeros of $B_+(E)$ exist.

(overwhelmingly usually at least)

So we've proven that bound ~~states~~ energy eigenstates in 1-d must be quantized if $V_\infty = 0$ {or a constant (V_0), In which case one case $\kappa_{\pm\infty} = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$ and everything ~~proceeds~~ proceeds in the same way.

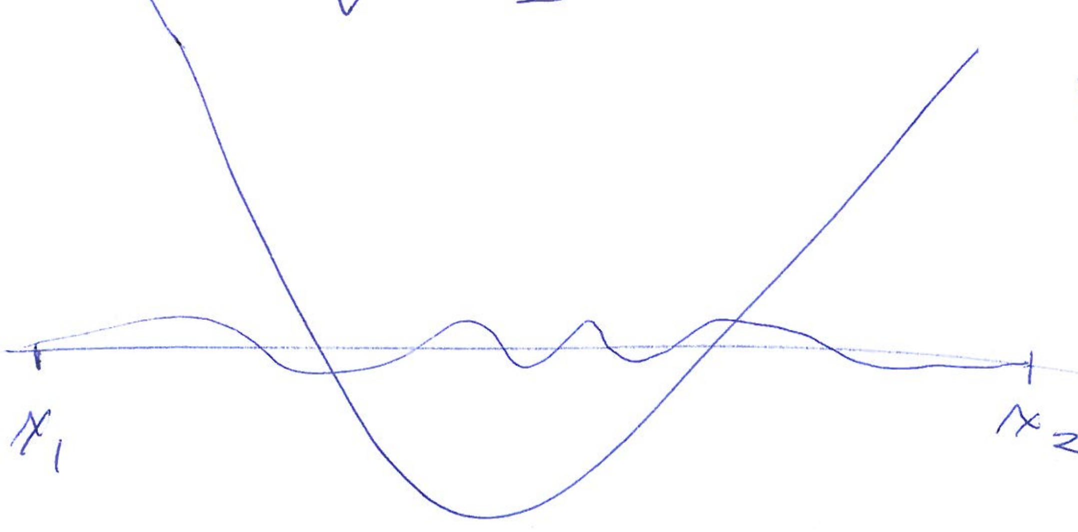
Holes in proof?

b) What if $V(x \to \pm\infty)$ doesn't level off to a constant? It could rise forever like the SHO potential

$$V = \frac{1}{2} k x^2 = \frac{1}{2} m \omega^2 x^2 .$$

(CT-483)

SHO ~~bound~~ stationary states are quantized by actual solution.



actual solutions go like $e^{-x^2/2\sigma^2}$ as $x \to \pm\infty$

So never like $e^{\pm\kappa|x|}$ over any region (Gr-56)

5-418

~~Well I think everything in the~~

Well one could still write down

$\psi(x_1) = A e^{\kappa x}$ for vicinity of x_1

$\psi(x_2) = B_+ e^{\kappa x} + B_- e^{\kappa x}$

for vicinity of x_2

but now $K = \sqrt{\frac{2m}{\hbar^2}(V - E)}$ is definitely a function of x.

The vicinities of x_1 and x_2 would be small if V varied strongly with x near there.

One could still look for $B_+(E) = 0$,

but now one can't be sure ~~that there are NOT~~ that this will ensure normalizability because the potential could change in non-monotonic way both for $x < x_1$ and $x > x_2$.

But look.

$$\kappa = \sqrt{\frac{2m}{\hbar^2}(V - E)}$$

If $V(x \to \pm\infty) = \infty$,

then $\kappa \to \infty$ as $x \to \pm\infty$.

The growing solutions as $x \to \pm\infty$ must be ruled out.

$\therefore$ $\chi(x = \pm\infty) =$ constant.

Actually $\chi(x = \pm\infty) = 0$ for normalizability and we already knew that.

$\boxed{5-420}$

~~I'd say for some~~

~~$x_1 < x_0 < x_2$~~

~~that~~

OK, let's try another tack.

The infinite square well and the SHO potential have quantized eigenstates by actual exact solution.

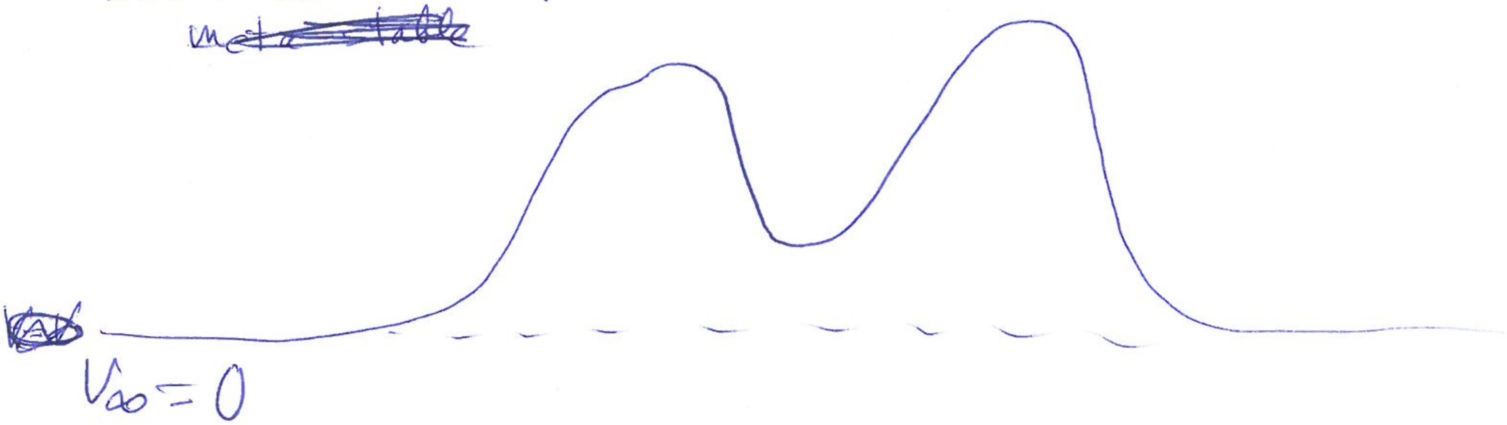
Imagine continuously deforming either one (but retaining $V(x \to \pm\infty) \Rightarrow \infty$) into any other shape.

Could the discrete set of solutions merge to form a continuum of solutions?

Can't imagine how,
but that's NOT
a proof.
Discussion breaks
off inconclusively.

6) What of wells
with $V_{min} > V_{\infty} = 0$?

Let's call them ~~metastable~~ quasi-wells



Can these ~~metastable~~ quasi wells
have bound states?
Classically yes. Obviously.
But in QM if $E > V_{\infty}$ never
exactly.

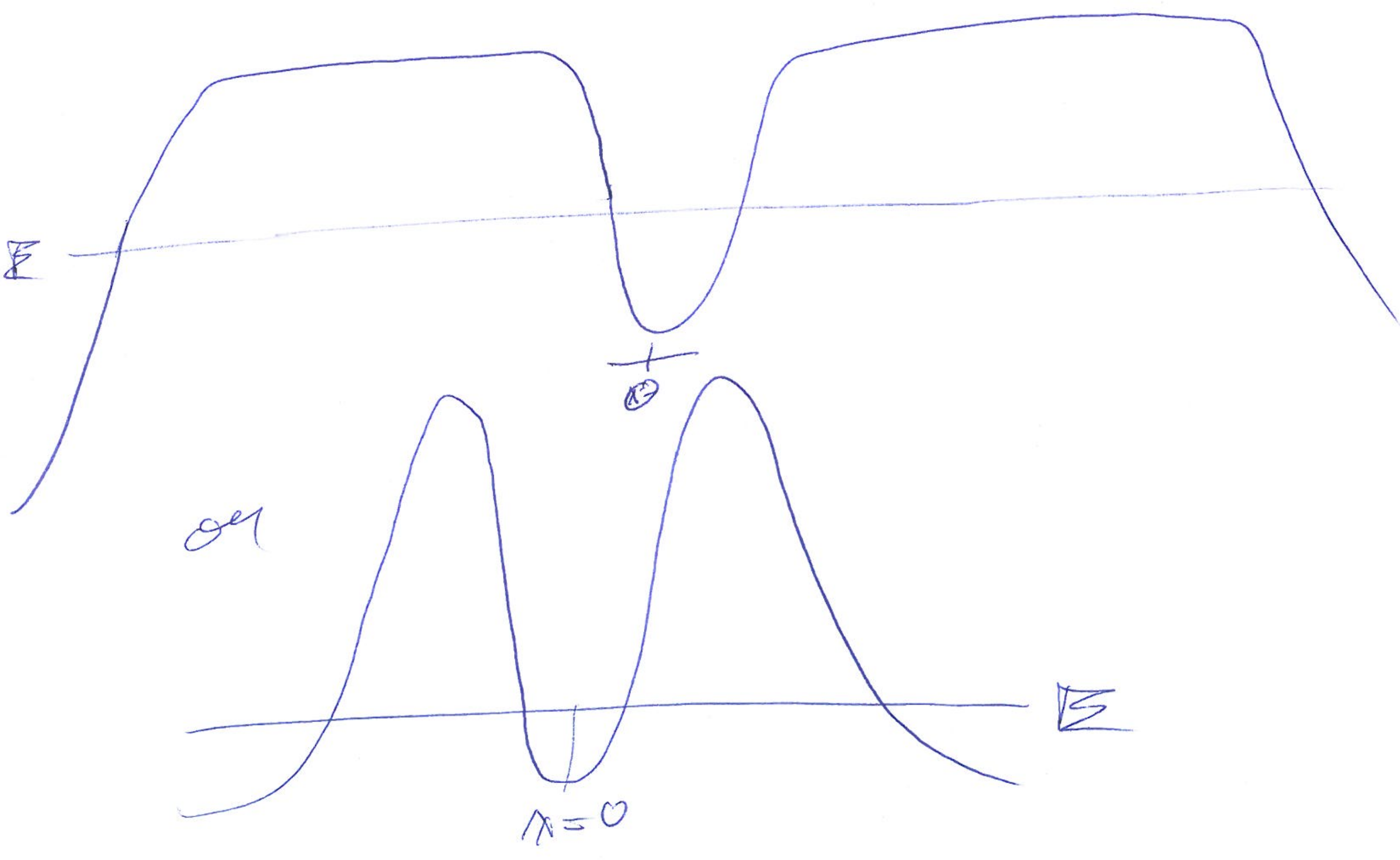
5 - 422

— There can always be QM tunnelling.

But there can be quasi-bound states

Are these quantized? ? in any sense?

I think yes. Imagine: ~~metastable~~ quasi- wells



By our (a) proof

and our (b) argument

~~(a bit handwavy)~~

(and a bit of handwaving),

there must be a continuum bands

~~limit band~~ of solutions

centered on certain

E values

that decline strongly

away from the ~~w~~

metastable well centered

where $E < V$

~~quasi bound state~~

quasi-stationary states.

— but others that grow strongly can also exist.

— for $|x| >> 0$, ~~the~~

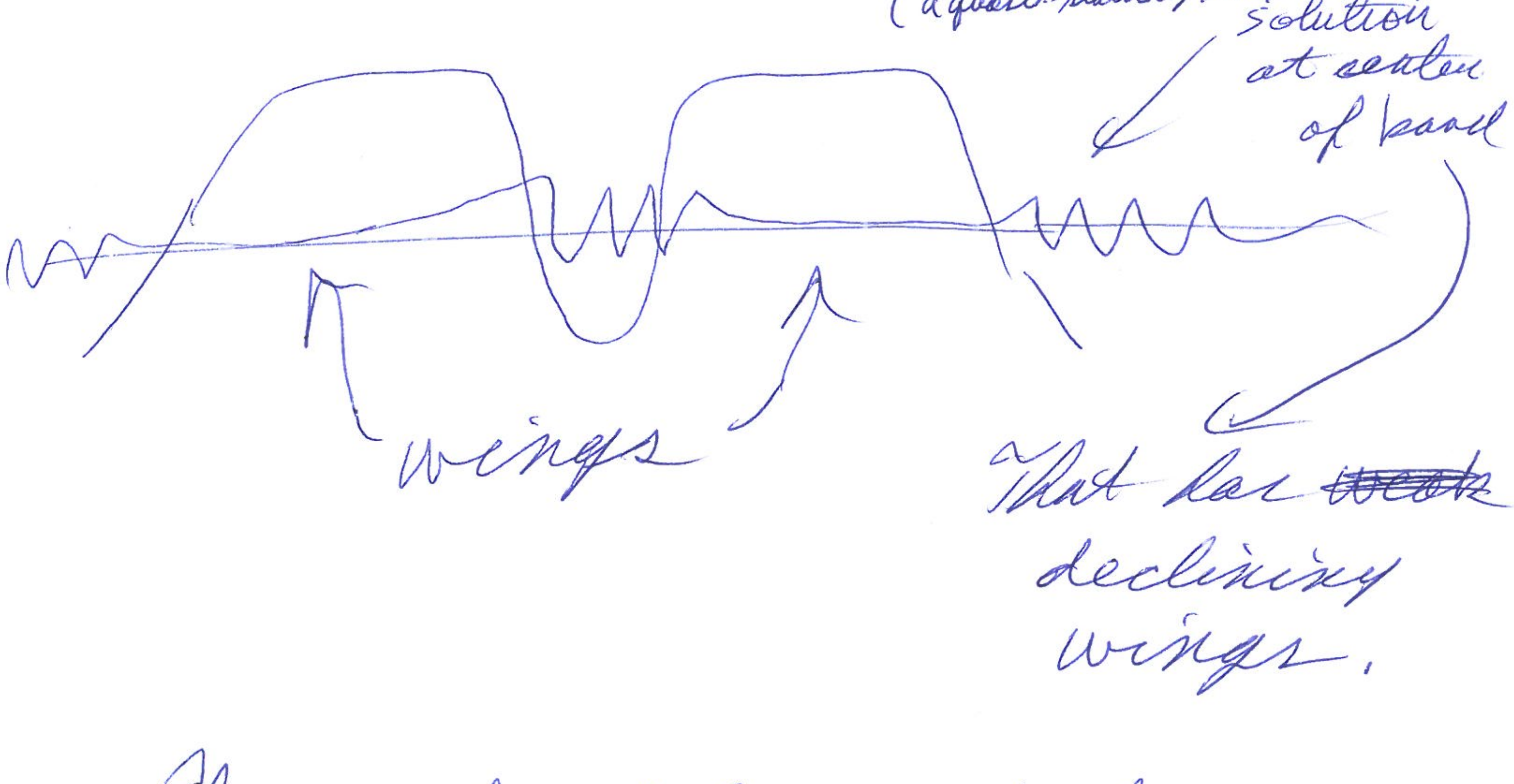
are in a region of

$E > V$ again and

5-424)

we have oscillatory solutions.

— I think all true solutions for the $(-\infty, \infty)$ region must be an unnormalizable continuum of solutions that are oscillatory as $x \to \pm\infty$.



Now a particle must be in a continuum linear combination of eigenstates—

— i.e., it must be in a wave packet since no ~~f~~unbound particle state is normalizable.

But it can be in packet

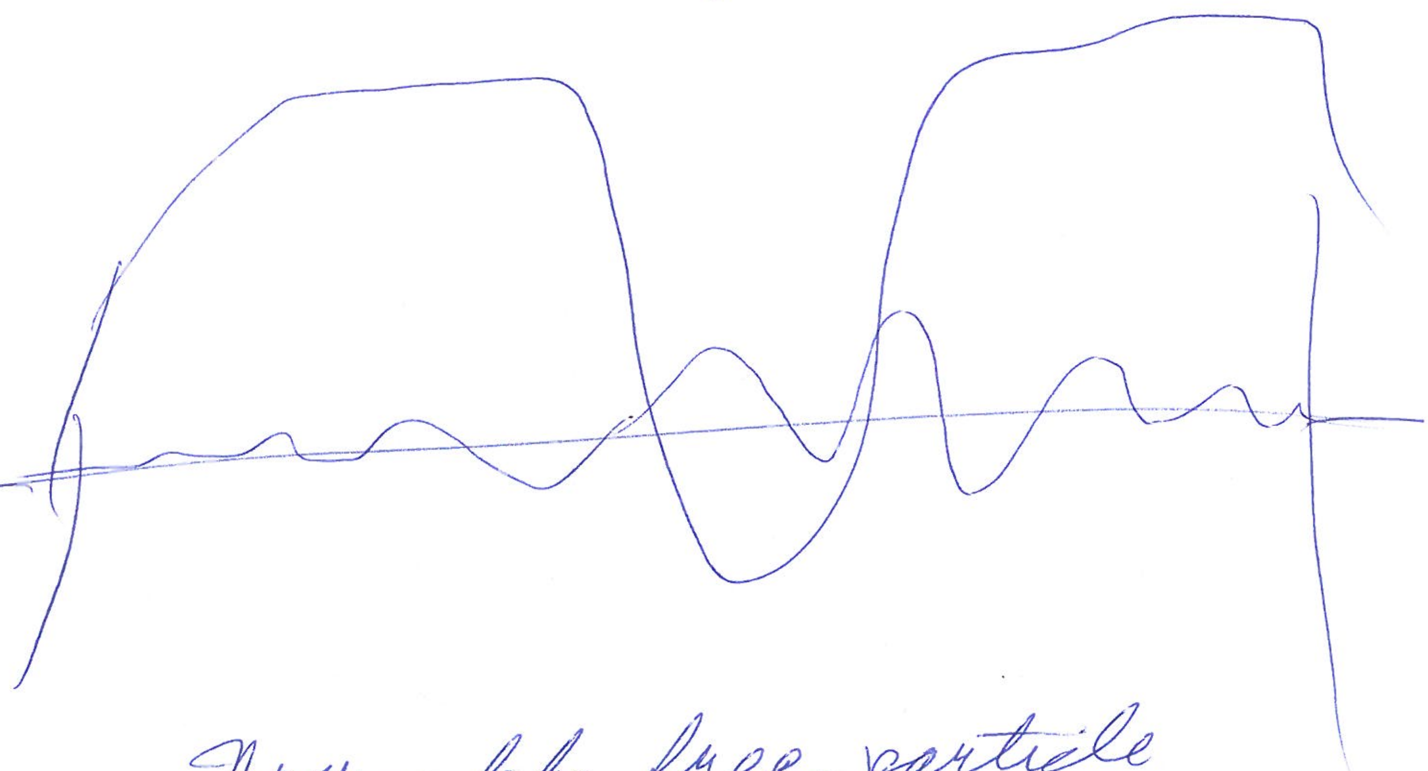
$$\psi = \int f(k) \underbrace{\phi_k(x)\, dk}_{\text{a wave number like quantum number.}}$$

where $f(k)$ peaks at a quasi-stationary state.

~~Will~~ to give ~~for~~ a quasi-stationary ψ or a mixture of quasi-stationary ψ's.

5-426a

~~How~~ I would guess, but not really know that this packet would ~~spread~~ ~~only ve~~ be centered in ~~metastable~~ quasi-well



— Now like free particle wave packets, it should spread out forever I think.

5-426b

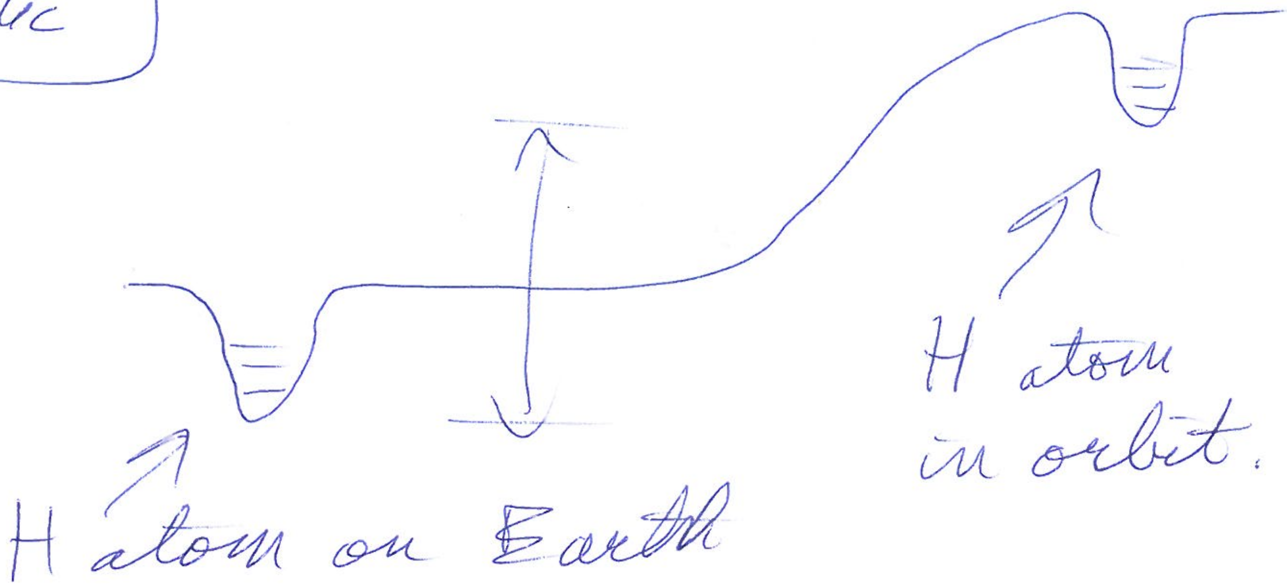
So eventually, the probability of being in the ~~metastable~~ quasi-well would be small.

<u>But</u> wave function collapses due to perturbations could collapse wave function <u>in</u> or <u>out</u> of the well.

Perhaps collapses <u>in</u> the quasi-well happen all the time making the ~~the~~ quasi-stationary state nearly exactly a stationary state. Actually the world is all ~~metastable~~ quasi-wells ~~states~~ ~~of mixed state~~

QM zero effect.

5-426c



$\Delta PE = mgx \simeq 10^{-30} \cdot 10 \cdot 10^{6}$ for example for one electron

$= 10^{-24}\ J$ difference in gravity

$\simeq 10^{-5}\ eV$

Small, but not minute.

Discussion breaks off inconclusively. Some great mind has thought it all through.

[Maybe exponentially declining eigenstates does actually just go to zero after awhile in a finite potential. Breaks ordinary QM rules though]

5-427

~~forever~~

So eventually probability density in metastable well would be small.

But wave-function collapses ~~could~~ due to perturbations ~~both~~ could collapse it to localize the particle <u>in</u> or <u>out</u> of the metastable well.

Probably collapses localizing in the well also tend to be collapses to quasi-stationary states rather than quasi-stationary states.

~~I don't know but somebody has worked all this out.~~

d) <u>Quantized States in Multi dimensions</u>

It seems plausible that if 1-d bound states must be quantized, so must multi-d bound states.

<u>But</u> many properties are

5-429

~~Atoms~~
~~many properties~~
~~are~~ a

functions of dimensionality,
and so ~~that~~
is a weak argument.

We know multi-d
rectangular Boxes infinite square well
and hydrogenic
atoms have
quantized eigenstates.

So ~~that~~ supports
general multi-d
quantization.

But a general proof
looks tough.

T-430)

Even CT-352 regard ~~that~~ as unspeakable.

(The boundary condition are a continuum not just two points as in 1-d)

Maybe an argument by *deformation* works.

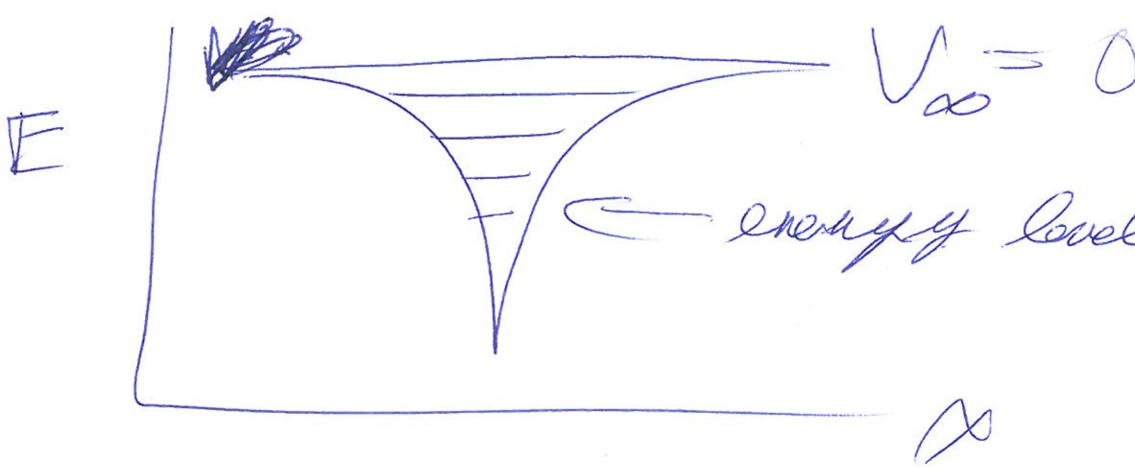
– Start from potential wells with known *exact* ~~quantized~~ *solutions* or at least *known quantized* solutions and imagine deforming ~~them~~ ~~into~~ those wells into any shape.

It seems unlikely that a continuum of ~~energy~~ energy eigenstates could ~~not~~ appear.

But there may be pathological cases ideally — maybe in reality.

3) Crude Idea of Why Solids are Bound

Isolated atoms are bound systems — bound even if neutral



- Nuclear forces binds up protons & neutrons into a lump of positive charge of size scale $\sim 10^{-15}$ to 10^{-14} m

- An equal amount of negative charge in a cloud

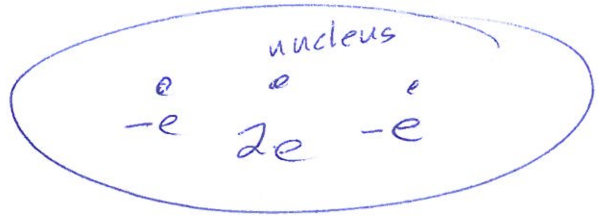
5 - 432

of electrons is bound to ~~that~~ nucleus.

How can an overall neutral atom be stable — tightly bound?

Arrangement counts as well as total charge.

e.g.,

He 

in classical picture.

— the nucleus can bind both electrons if they keep relatively far apart.

— ~~negative ions~~

— and so in general for neutral ~~at~~ atoms

— positive ions are even more tightly bound

— negative ions can form ~~too~~ e.g., H^- which is an important source of opacity in Sun.

Mihalas — 103

If you bring atoms together with low enough temperature (which can be quite high in some cases: Tungsten T = 3695 K under ordinary pressure) and high enough (which can be zero), they will bind into solids.

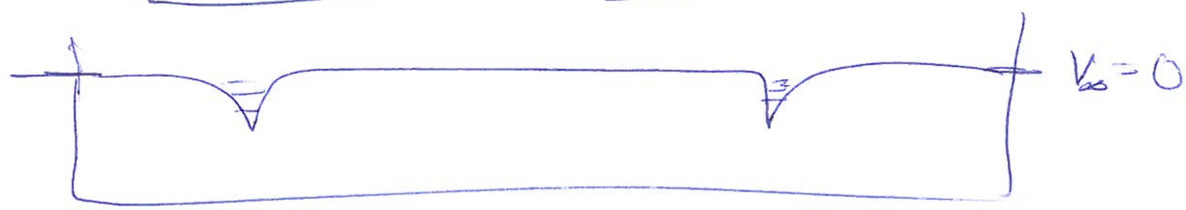
— everyday things we call solids are often quite solid.

Crudely speaking when you bring atoms together, their electron wave functions ~~can~~ will overlap and reform into binding wave functions that glue the atoms together.

The outermost electrons stationary wave functions become de-localized.

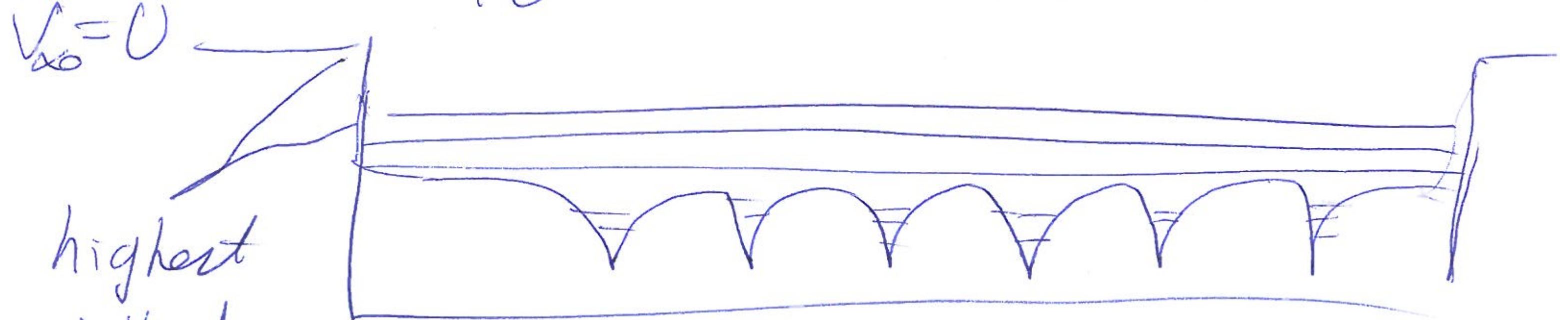
In a single-particle sense of wave functions

Cartoon atoms far apart



to

atoms squashed together.



highest filled stationary single particle states are well below $V_\infty = 0$ level for tightly bound solids.

Arrangement again leads to tight bonding. Made possible by nuclear force binding positive charge in the nucleus.

— the inner~~most~~ atomic single particle states stay separate and localized at ~~(except in~~ least to a very good approximation

(all states in the universe are delocalized in the ideal QM limit — which is well beyond our ability to test)

Only the outermost stationary states ~~or~~ ~~or~~ valence states merge into delocalized states.

5-436

How delocalized?
Well whole sample
of solid in principle.
But maybe inner boundaries
cause some localization.
Maybe grain boundaries
sometimes
(grains = crystallites
→ defective boundaries
~~pa~~ between lumps of
regular lattice structure
— typically grain size
from nanometers to
millimeters
but larger ones are
possible up ~~to~~ to .5 m for
an ice crystallite (Wik)

[5-437

But localization is always relative in QM

(good approximation,
extremely good approximation,
experimentally indistinguishable
from true locatization

<u>or</u>

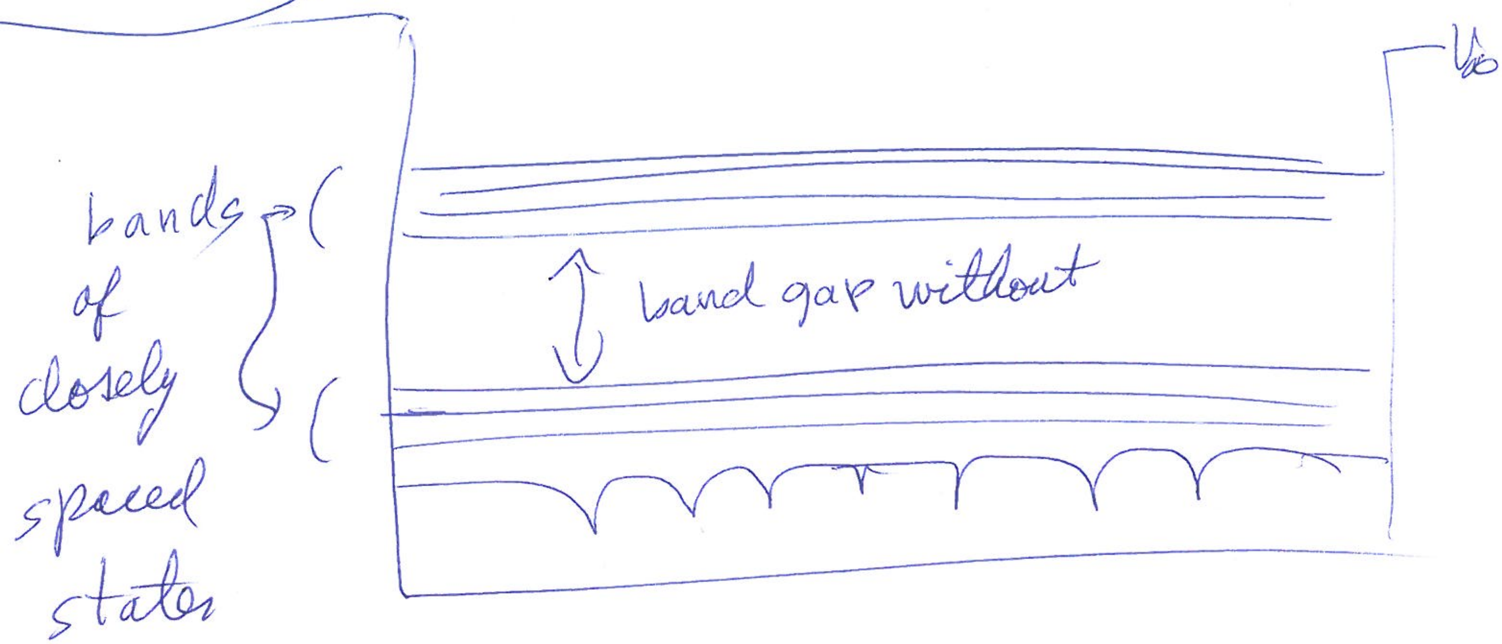
bad approximation
or hopeless).

~~Thus~~ In regular lattice solids, ~~there~~ is a <u>periodic potential</u> (at least over the grains)

and that leads to <u>band structure</u>

of the delocalized states.

5-438



In ground state of solid electrons occupied states up to the Fermi surface of constant single-particle state energy.

→ If the Fermi surface occurs in a band gap that is large ~~broad~~, the solid is an insulator.

If the band gap ≲ 2eV (ER-467) the solid is a semi-conductor

If the Fermi surface
is in a band of states,
the conduction band it is called
the solid is a conductor.

The reason for these
differences, is that
causing electrons to
form traveling wave packets
takes energy to ~~promote~~ excite the electrons to a traveling state.
— in the ground state
the net motion is
zero.

In ~~an~~ conductor, this energy
is vanishingly small.
In an insulator, it is large.
In a semi-conductor, it is intermediate
thermal energy will excite

5-44U

some electrons

— So semi-conductor conductivity increases with temperature

[amorphous solids like glass are another story that I'll skip here]

For many solid state purposes, you only need to deal with the delocalized states (free electrons) with a periodic potential (for regular lattice solids)

for bottom of solid well