| 11 | Wed., 11/12
Fri., 11/14 | **5.3** Solids (Unit T7.2)
8.1-.2 WKB Approximation & Tunneling | **Daily 11.W**
Daily 11.F |
| 12 | Mon., 11/17
Tues. 11/18 | **6.1** Time-independent Perturbation, non-degenerate | **Daily 12.M**
Weekly 12 |

Daily: Kyle Jacob   Spencer   Gigja   Anton   Jessica   Sean   Antwain   Jonathan Casey   Jeremy   Mark Connor   Brad

Equipment
- Griffith's text
- Moore's Text
- Thornton & Rex Ch. 8 - Atoms

Check dailies

Announcements

Daily 11.W Wednesday 11/12
1. *Math*: Griffiths 5.15
2. *Starting Weekly HW*: Griffith 5.16
3. *Starting Weekly HW*: Griffiths 5.18

5.   Identical Particles

5.3   Solids

The Pauli Exclusion Principle (that two fermions can't be in the exact same state – all the way down to same spin) plays a key role in 'filling up' atoms and collections of atoms – solids.

As I always tell folks in General Physics I, while Physicists are principled enough love our fundamental principles and absolutely right laws, we're also practical enough to appreciate approximating things when that's 'good enough' for answering the question at hand. The two models that are explored in this section are 'good enough' for getting at some pretty important properties of solids.

Say you have two atoms with only partially-filled outer electron orbitals, like iron with its 6 (instead of 10) electrons in the $3d$ ($n=3$, $l = 3$) level. If you brought another iron atom quite near, the electrons in their outer level, known as the 'valance' level, would happily form a new, extended orbital that encircles both atoms. Bring in another atom, and another,… and you can have a giant 'orbital' that links all the atoms that make up a solid.

Of course, the new situation is rather complicated, but we can learn some of its basic properties by considering the simplest and second-simplest approximations:
     The Free Electron Gas
     The simple Periodic Potential

5.3.1 The Free Electron Gas

To 0th order, from the perspective of one electron in this solid, all the other electrons and all the protons in the nucleus all but cancel each other out; the electron's trapped in the solid, but other than that, it's free to zip around however it wants within the solid – like a gas particle in a box.

Okay, say we have an electron in a 3-D box of dimensions l_x, l_y, l_z. The potential it experiences is

$$V(x, y, z) = \begin{cases} 0 & \text{in box} \\ \infty & \text{out of box} \end{cases}$$

So we just have the old 3-D infinite-square well

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m}$$

$$\frac{\hbar}{i}\frac{\partial}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2}$$

As the terms are separated, the solution is separable.

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

To make life particularly simple, let's take the origin to be the bottom back left corner. We know each factor in the solution looks like then

$$\psi(x, y, z) = \left(\sqrt{\tfrac{2}{l_x}}\sin(k_x x)\right)\left(\sqrt{\tfrac{2}{l_y}}\sin(k_y y)\right)\left(\sqrt{\tfrac{2}{l_z}}\sin(k_z z)\right) = \left(\sqrt{\tfrac{8}{V}}\sin\left(\tfrac{n_x \pi}{l_x} x\right)\sin\left(\tfrac{n_y \pi}{l_y} y\right)\sin\left(\tfrac{n_x \pi}{l_z} z\right)\right)$$

Where each n can be 1,2,3,4,…

Now, the energy of the electron in such a state would be

$$E\psi_{n_x n_y n_z} = \left(\frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m}\right)\psi_{n_x n_y n_z}$$

$$E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

Fermi Energy

This would be helpful. I'm just not sure where he starts the whole derivation.
Mark T, Redlands, CA

And each possible spatial state, specified by n_x, n_y, n_z, can have only 2 electrons, corresponding to the additional degree of freedom's, spin's, two possible alignments. So if we had a collection of N_e electrons, then what would be the highest energy an electron would have to have / the highest energy state that would have to be occupied? That's known as the Fermi Energy.

In "k space", we can easily map out the possible states and then imagine filling them up.
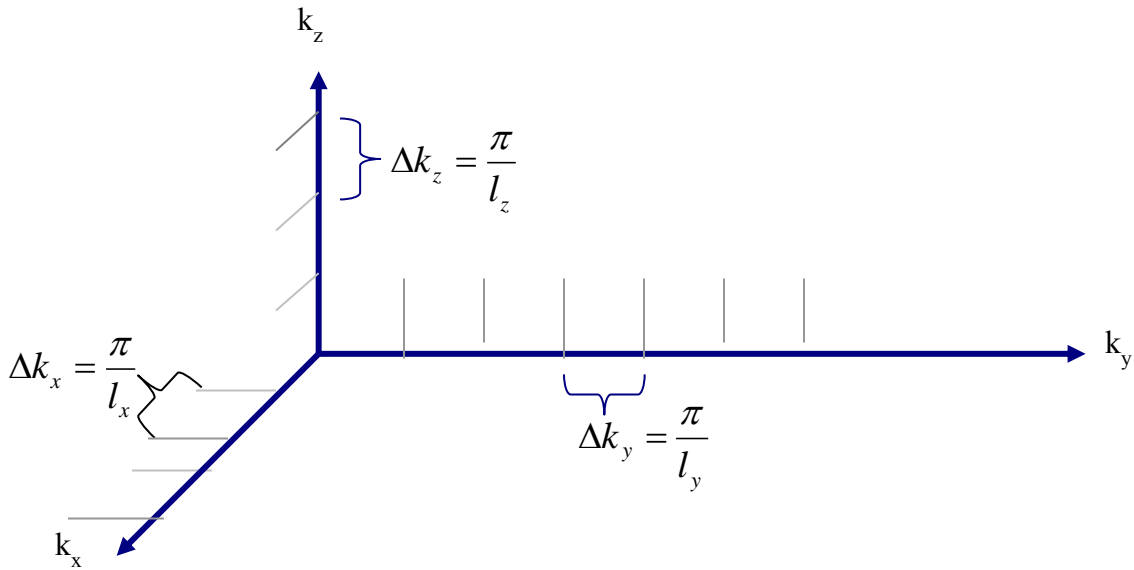
You can specify any allowed state with a point of allowed k_x, k_y, and k_z, or the intersections of a grid in k space.
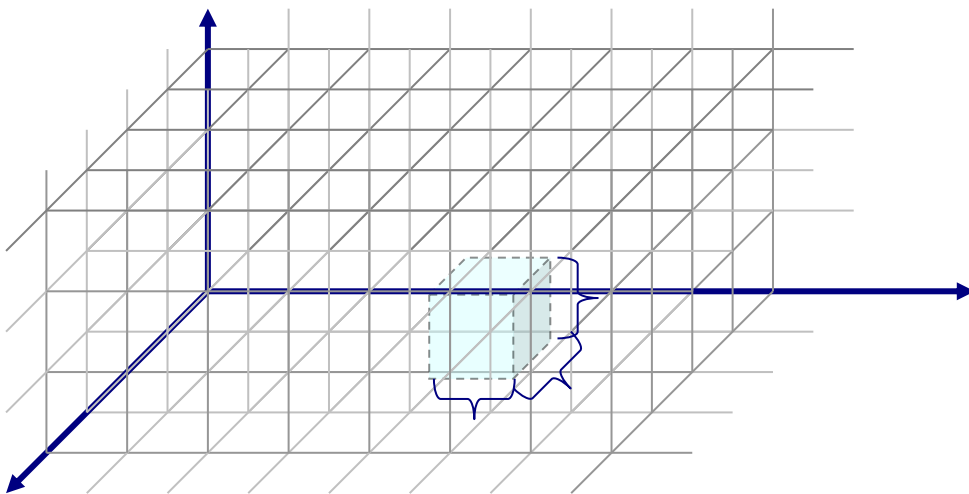
Now, in this grid space, there are two (for spins) allowed electron states per step in k_x, k_y, k_z. This can be phrased as a 'density of states' if you will of

$$\frac{2\,states}{\Delta V_k}$$

where

$$\Delta V_k = \Delta k_x \Delta k_y \Delta k_z = \frac{\pi^3}{V}$$

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Of course, this ratio of number of states to volume in k-space must be the same as the *total* number of electrons to the *total* volume of occupied states.

$$\frac{2\,states}{\Delta V_k} = \frac{N_e}{V_k}$$

Now, we're talking a *whole* lot of electrons, so the discrete step sizes from one allowed to another allowed k state are infinitesimal in comparison to the largest k value for an occupied state, which we'll call k_F. In other words, it's a pretty good approximation to treat k as a continuous variable, and so say that

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right),$$

or more suggestively

$$\sqrt{2mE_F}\,/\hbar = k_F = \sqrt{k_x^2 + k_y^2 + k_z^2}\ ,$$

Is the radius of a sphere in k-space; all states with k combinations that lie within that sphere are occupied; all outside that sphere are empty.

Of course, the volume of a sphere of radius k_F is $V_{k.sphere} = \frac{4}{3}\pi k_F^3$, but looking at our grid of allowed states, we only have positive k components, so only the positive octant of the sphere encloses states.

$$V_k = \frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{1}{6}\pi\left(\sqrt{2mE_F}\,/\hbar^2\right)^3 = \frac{1}{6}\pi \frac{\left(2mE_F\right)^{3/2}}{\hbar^3}$$

Putting all this together,

$$\Delta V_k = \frac{\pi^3}{V} \qquad\qquad\qquad V_k = \frac{1}{3}\pi m E_F$$

$$\frac{2\,states}{\Delta V_k} = \frac{N_e}{V_k}$$

$$\frac{2}{\dfrac{\pi^3}{V}} = \frac{N_e}{\dfrac{1}{6}\pi \dfrac{\left(2mE_F\right)^{3/2}}{\hbar^3}}$$

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N_e}{V}\right)^{2/3}$$

or relating that to the number of atoms in the solid, if each of N atoms has q electrons in its valance level to contribute to this 'electron gas', then

$$N_e = qN$$

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 q \frac{N}{V}\right)^{2/3}$$ from which, incidentally, it's easy to identify

$$k_F = \left(3\pi^2 q \frac{N}{V}\right)^{1/3}$$

> I'm not sure on why he had to define another density for Equation 5.42, could we go over that part as well?
> Jeremy, Redlands, CA

As you'll see in Statistical Mechanics, the Fermi energy comes into a lot of arguments about how the population of electrons behaves.

> Can we go over the derivations starting at 5.41and ending at 5.46 for degeneracy pressure? I got lost on how he found the equations in this derivation" Jessica
>
> I got lost here too. Jonathan
> I would also like to review this in class. Also, after those eqs he briefly mentions how they are a partial answer to the question as to why a solid doesn't collapse on itself. Why was this a concern in the first place? Jacob C,

Ground State Energy
Something we can fairly easily do at this point is figure out the ground state energy for the whole system. In principle, that's simply the sum of the energies for each of the occupied states,

$$E_{total} = \sum_{state}^{occupied} E_{state}$$

We can re-parameterize that sum as being over all states in k space, times their energies

$$E_{total} = \sum_{k}^{k_F} E(k)\frac{states}{\Delta V_k}\Delta V_k \Rightarrow \int_0^{k_F} E(k)\left(\frac{states}{\Delta V_k}\right)dV_k$$

Taking the steps in k-space between allowed states to be infinitesimal in comparison to k_F, we can approximate this discrete sum as an integral.

Again, the density of states per bit of volume in k-space is $\Delta V_k = \frac{\pi^3}{V}$. Now, all points in k space that have the same magnitude of k have the same energy, $E(k) = \frac{\hbar^2}{2m}k^2$, so we easily do this integral in spherical coordinates since, though just over the positive octant again.

$$E_{total} = \int_0^{k_F} \frac{\hbar^2}{2m}k^2\left(\frac{2}{\frac{\pi^3}{V}}\right)\tfrac{1}{8}\left(4\pi k^2\right)dk = \left(\frac{V\hbar^2}{2m\pi^2}\right)\int_0^{k_F} k^4\,dk = \frac{1}{5}\left(\frac{V\hbar^2}{2m\pi^2}\right)k_F^5$$

Or substituting $k_F = \left(3\pi^2 q \dfrac{N}{V}\right)^{1/3}$

$$E_{total} = \left(\frac{V\hbar^2}{10m\pi^2}\right)\left(3\pi^2 q \frac{N}{V}\right)^{5/3} = \left(\frac{\hbar^2}{10m\pi^{1/3}}\right)\frac{(3qN)^{5/3}}{V^{2/3}} = \frac{3qN}{5\pi^{5/3}}\left(\frac{\hbar^2}{2m}\right)\left(3\pi^2 q \frac{N}{V}\right)^{2/3} = \frac{3qN}{5\pi^{5/3}} E_F$$

Given that the number of electrons in the 'gas' is qN, we can say that the average energy per electron is $E_{ave} = \dfrac{E_{total}}{qN} = \dfrac{3}{5\pi^{5/3}} E_F$

> "I'd like to go over how Griffiths gets to the degeneracy pressure. I'm confused where this "pressure" comes from." Spencer
>
> I do not understand the concept of the degeneracy pressure. I think it would be nice to go over this briefly in class. Kyle B,

Notice that the energy expression depends on the volume. That's not terribly surprising; for an individual state, the energy depends on the dimensions of the 'box' the electron's trapped in – the wider the box, the broader the wavelength, the lower the energy. So it's not terribly surprising that it would take work to compress the box, or that this 'gas' exerts a pressure. Put in thermodynamic terms, the work associated with changing a volume in spite of a pressure is

$$\Delta E_{total} = W = -P\Delta V$$

So, in the differential limit,

$$P = -\frac{dE_{total}}{dV} = -\frac{d}{dV}\left(\frac{\hbar^2}{10m\pi^{1/3}}\right)\frac{(3qN)^{5/3}}{V^{2/3}} = \frac{2}{3}\left(\frac{\hbar^2}{10m\pi^{1/3}}\right)\left(\frac{3qN}{V}\right)^{5/3} = \frac{2}{15\pi}\left(\frac{\hbar^2}{2m\pi^{1/3}}\right)\left(\frac{3qN}{V}\right)^{5/3}$$

While this is called the Degeneracy Pressure, Griffiths notes that it might better be called the 'exclusion pressure'. Of course, even if we had Bosons, and all particles were in the lowest possible state, there'd still be a pressure like this, though not as large, since changing the size of the 'box' would still spread wavelengths and lower energy or compress and raise energy.

5.3.2 Band Structure

> "Why is the dirac comb even a possible model at all?" Casey P,
>
> I would assume it's not a possible model in the sense that a real solid like this can exist(No one dimensional string of atoms), but it is an oversimplification that allows us to approach and better understand the model for a real solid? Jacob C,

The next simplest model is to allow that these valance electrons probably *do* notice the periodic placement of the atoms, and so would experience a periodic potential. Just to show how

periodicity leads to bands of allowed states, Griffiths looks at the simplest imaginable periodic potential – a 1-D line of delta-potentials that wraps around on itself.

If the separation of the delta-spikes is *a,* (he suggests that spikes are easier to deal with than wells, but we can imagine those as the *borders* between atoms if we want)

$$V(x)=V(x+a) \text{ or more specifically, } V(x)=\sum_{j=0}^{N-1}\delta(x-ja)$$

Of course,

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

$$\frac{\hbar}{i}\frac{\partial}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)$$

Now, given the periodicity, it must be that all measurable are also periodic: that means both the probability density and the energy. Of course, that constrains the wavefunction to be periodic *to within a phase.*

$$\psi(x+a)=e^{i\gamma}\psi(x)$$

Note that the latter requires that the phase factor *not* depend upon x (otherwise it get acted upon by the derivative in the Hamiltonian and yield new energies.)

"I get 5.52 and 5.53 individually, but I don't really understand the jump. Am I supposed to just accept it? I thought I understood it when I thought the wave function was periodic, but in fact, the wave function is not itself periodic."Gigja

Using eq 5.49 and subbing in for Psi(x+a) you get e^(ika)Psi(x) = Lambda * Psi(x) leading do 5.53
I think this is was using Bloch's theorem. Jacob C,

To make life really simple, we imagine that we have a ring of N steps of length a, then looping all the way around would bring you back to where you started and looking at the exact same wavefunction:
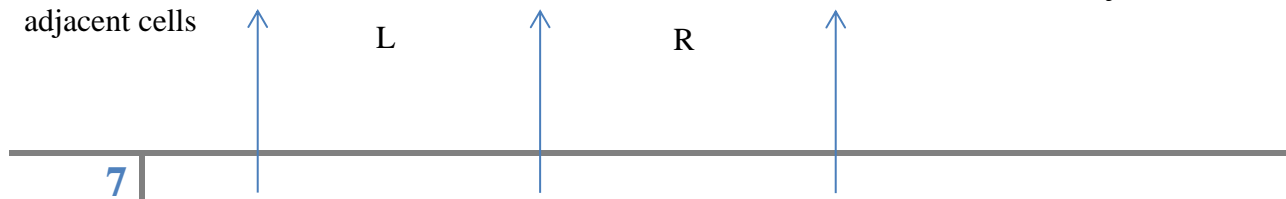
$$\psi(x+Na)=\left(e^{i\gamma}\right)^N\psi(x)=\psi(x)$$

So it must be that $e^{iN\gamma}=1$ or $N\gamma=n2\pi \Rightarrow \gamma=\frac{n2\pi}{N}$ for $n=\pm 0,1,2,3,\ldots$

So,

$$\psi(x+a)=e^{in\frac{2\pi}{N}}\psi(x) \text{ for } n=\pm 1,2,3,\ldots$$

Now that we know how solutions translate from one 'cell' to the next, let's focus on just two adjacent cells

L   R

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-a   0   +a

$$\frac{\hbar}{i}\frac{\partial}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \frac{\hbar}{i}\frac{\partial}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\psi_R(x) = Ae^{ikx} + Be^{-ikx} \text{ where } E = \frac{-\hbar^2 k^2}{2m}$$

Note: Griffiths had guessed Sines and Cosines, which are perfectly general too, but since we typically *don't* it felt a little contrived. So I guessed exponentials, that works too.

Then the relation between the wavefunction evaluated in the region to the right and in the region to the left is $e^{in\frac{2\pi}{N}}\psi_L(x) = \psi_R(x+a)$ or

$$\psi_L(x) = e^{-in\frac{2\pi}{N}}\left(Ae^{ik(x+a)} + Be^{-ik(x+a)}\right)$$

Boundary conditions

$$\psi_R(0) = \psi_L(0) \qquad\qquad \frac{d\psi_R}{dx}\bigg|_0 - \frac{d\psi_L}{dx}\bigg|_0 = \frac{2m\alpha}{\hbar^2}\psi(0)$$

$$A + B = e^{-in\frac{2\pi}{N}}\left(Ae^{ik(a)} + Be^{-ik(a)}\right) \qquad ik(A-B) - ike^{-in\frac{2\pi}{N}}\left(Ae^{ik(a)} - Be^{-ik(a)}\right) = \frac{2m\alpha}{\hbar^2}(A+B)$$

So,

$$\frac{A}{B}\left(1 - e^{-in\frac{2\pi}{N}}e^{ik(a)}\right) = e^{-in\frac{2\pi}{N}}\left(e^{-ik(a)}\right) - 1 \qquad \left(\frac{A}{B}-1\right) - e^{-in\frac{2\pi}{N}}\left(\frac{A}{B}e^{ik(a)} - 1e^{-ik(a)}\right) = \frac{2m\alpha}{ik\hbar^2}\left(\frac{A}{B}+1\right)$$

$$\frac{A}{B} = \frac{e^{-in\frac{2\pi}{N}}\left(e^{-ik(a)}\right) - 1}{\left(1 - e^{-in\frac{2\pi}{N}}e^{ik(a)}\right)} \qquad\qquad \frac{A}{B} = \frac{\frac{2m\alpha}{ik\hbar^2} + 1 - e^{-ik(a)}e^{-in\frac{2\pi}{N}}}{\left(1 - e^{-in\frac{2\pi}{N}}e^{ik(a)} - \frac{2m\alpha}{ik\hbar^2}\right)}$$

Combining

$$\left(e^{-in\frac{2\pi}{N}}\left(e^{-ik(a)}\right) - 1\right)\left(1 - e^{-in\frac{2\pi}{N}}e^{ik(a)} - \frac{2m\alpha}{ik\hbar^2}\right) = \left(1 - e^{-in\frac{2\pi}{N}}e^{ik(a)}\right)\left(\frac{2m\alpha}{ik\hbar^2} + 1 - e^{-ik(a)}e^{-in\frac{2\pi}{N}}\right)$$

$$\boxed{\cos(ka) + \frac{m\alpha}{k\hbar^2}\sin(ka) = \cos\left(n\frac{2\pi}{N}\right)}$$

Cleaning this up as Griffiths does,

$$z \equiv ka \text{ and } \beta \equiv \frac{m\alpha a}{\hbar^2}, \text{ we'd have}$$

$$\cos(z) + \beta\, \frac{\sin(z)}{z} = \cos\left(n\,\frac{2\pi}{N}\right)$$

Where the point is that, only specific *k's* and thus corresponding energies, since $E = \dfrac{-\hbar^2 k^2}{2m}$, are allowed. Now, for N >> 1, cosine on the right virtually varies continuously, allowing virtually a continuum of possible values that the left-hand-side must equal, from 1 to -1.

However:
1. They *are* indeed discrete, so there are only *discrete* values allowed and
2. Cosine is bound by -1 and 1, whereas the left hand side isn't. Depending on

   $\beta \equiv \dfrac{m\alpha a}{\hbar^2}$, and thus the strength of the potential, the function can be outside the

   allowed range for whole swaths of k's. So, there are swaths, or "bands" of un-allowed k values.

Mathematically, this gives us 'bands' of allowed *k's* and thus *E's* , separated by 'gaps' of un-allowed energies.

Implications
To get a *physical* understanding of why this is and what the implications are, let's look at the thresholds between bands and gaps, when

$$\cos(z) + \beta\, \frac{\sin(z)}{z} = \cos\left(n\,\frac{2\pi}{N}\right) = \pm 1$$

Filled, partly filled, and vacant bands – Conductors and Insulators
First off, that happens for $n = \pm N/2$, N, 3N/2,… so, within a band we can satisfy this equation for *n = 0 to N-1*. So there are N/2 possible versions of this equation that *z can* satisfy, where N is the number of atoms in our periodic 1-D solid ring. Now, if you plot out this function, you'll find that there are generally 2 values of *z,* thus 2 *k's* that satisfy each version of the equation. So there are 2N/2 or N states.

Now, if we throw in that we're dealing with electrons that also have the 2 spin degrees of freedom, we'd have a total of 2N possible states per band.

How many electrons do we have to populate these bands? Harkening back to free electron gas model, if N is the number of atoms, and each has q electrons in its valance orbital, then then $N_e = qN$ is the number of electrons that can be shared among atoms. So:
    If q = 1, the first band is ½ full.
    If q = 2, the first band is completely full
    If q = 3, the second band is ½ full
    …

A qualitative implication is that, if a band is full (q is even), then it would take a large bump in energy to promote an electron from the state it's in to the next available, un-occupied state, whereas, if a band is only ½ full (q is odd), then it would be pretty easy. Quantitatively, in real materials 'pretty easy' is well within range of random thermal jostling's while 'a large bump' is a few eV's.

If each state corresponds to a particular momentum, then having all available states filled means not being able to change the net motion of electrons in the material – it's an insulator; having a band only half-filled means it's much easier to change the state of motion of some electrons – it's a conductor.

The threshold
Still, what is it physically that means there's a huge jump in available energies?

Well, let's look at the top of the band, the threshold. It's not too hard to see what must be the case for $\cos(z) + \beta \dfrac{\sin(z)}{z} = \cos\left(n\dfrac{2\pi}{N}\right) = 1$

At z=ka = nπ. for n even. That kills the sin term and makes the cosine terms 1.
For that matter, at the bottom of the band,

$$\cos(z) + \beta \frac{\sin(z)}{z} = \cos\left(n\frac{2\pi}{N}\right) = -1$$

z=ka = nπ. for n odd. That also kills the sine term.

Now, in general, as you'll show in problem 5.19, the general wavefunction is As you'll show in 5.18, the wavefunctions are $\psi(x) = C\left[\sin(kx) + e^{-in\frac{2\pi}{N}} \sin(k(a-x))\right]$.

However, at the top of a band, where z=ka = jπ, and $e^{-in\frac{2\pi}{N}} = 1$, a lot of the work that gets to this wavefunction breaks down, and you have to go pretty far back to find that $\psi(x) = C\sin(kx)$, in other words, the wavefunction happens to be 0 right where there's a potential.

I haven't worked it out, but at the other end, I'm thinking we'll get $\psi(x) = C\cos(kx)$; that is, the wavefunction feels the potential most strongly.

That's the key to the gap – for the same k's you can get different energies if you're shifted to overlap a lot or a little with the potentials.