Infinite 1-D Lattice II

LAST TIME:

H_2^+ localization⟷tunneling: overlap ! bonding and antibonding orbitals

Internuclear distance, R, vs. $a_0 n^2$
Bohr radius for n[th] orbit in H atom

energy below top of barrier

TIGHT-BINDING (Kronig-Penney) Model (see Baym pp. 116-122)

1-D ∞ lattice: 1 state per ion!
tunneling only between nearest neighbors!
Infinite dimension **H** matrix

$$\mathbf{H} = \begin{pmatrix} E_0 & -A & \ddots & 0 \\ -A & E_0 & \ddots & 0 \\ 0 & \ddots & \ddots & \ddots \\ 0 & 0 & \ddots & \ddots \end{pmatrix}$$

$$\langle \nu_q | \mathbf{H} | \varphi \rangle = E \langle \nu_q | \varphi \rangle$$ left multiply both sides by $\langle \nu_q |$

$$|\varphi\rangle = \sum_{q=-\infty}^{\infty} c_q |\nu_q\rangle$$ Variational wavefunction. Minimize E.

$$0 = c_q (E_0 - E) - A(c_{q-1} + c_{q+1})$$ ∞ # of coupled linear equations, one for each q

Usually solve for $\{c_q\}$ by setting determinant of coefficients = 0, and then solve for E.
Can't do this because determinant is of ∞ dimension.

TRICK: expect equal probability of finding e^- on each lattice site by analogy to the plane wave e^{ikx}, where probability density is uniform at all sites along x.
Try:

$$c_q = e^{ikq\ell} \qquad x_q = q\ell$$

integer

distance between lattice sites

Notice that this is similar to free particle e^{ikx}, which seems rather strange because particle is never really free in the "tight-binding" model.

$\left|c_q\right|^2 = 1$

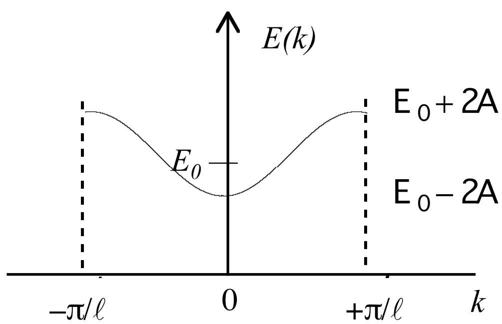
plug trial form for c_q into $0 = c_q\left(E_0 - E\right) - A\left(c_{q-1} + c_{q+1}\right)$

$$0 = e^{ikq\ell}\left(E_0 - E\right) - Ae^{ikq\ell}\left(e^{-ik\ell} + e^{+ik\ell}\right)$$

divide through by $e^{ikq\ell}$

$0 = \left(E_0 - E\right)k - A2\cos k\ell$

$\boxed{E(k) = E_0 - 2A\cos k\ell}$ E vs. k, we have achieved our goal!



maxima

minima

E varies continuously over an interval of 4A, where A is the adjacent site interaction strength or the "**tunneling integral**"

What happens when we look at k outside $-\pi/\ell \le k < \pi/\ell$, which is called the "1st Brillouin Zone"

$$c_k = e^{ikq\ell}$$

$$k' = k + \frac{2\pi}{\ell}$$

(one additional allowed wavelength per lattice spacing ℓ)

$$c_{k'} = e^{i\left(k+\frac{2\pi}{\ell}\right)q\ell} = e^{ikq\ell}\underbrace{e^{i2\pi q}}_{=1} = e^{ikq\ell}$$

wavefunction is unchanged!

So if k goes outside 1st Brillouin Zone, we get the same Ψ, so we get the same E.!
Nothing new!
No point in allowing k to vary more widely than $-\pi/\ell \le k \le \pi/\ell$.

Today's Lecture:

Unanswered Questions:

1. How many distinct orbitals are there in a band?

   N-atom periodic array. Try *Periodic Boundary* conditions:

   $$\left.\begin{array}{l}\text{longest } \lambda=\ell N \\ \text{shortest } \lambda=\ell\end{array}\right\} \text{N possible values of } \lambda = 2\pi/k. \text{ N atoms, N values of } k$$

   $$0 \approx \frac{2\pi}{\ell N} \le |k| \le \frac{2\pi}{\ell} \text{ in N steps of } \frac{2\pi}{\ell}$$

   infinite lattice: $\frac{-\pi}{\ell} < k < \frac{\pi}{\ell}$ contains all of the states generated from one state per atom.

2. What happens at $E > E_0 + 2A$?

   There is a gap – no states allowed
   What is the next higher state of each atom?
   Get a free particle (electron) if E > *work function* of the solid
   [energy required to remove e^- from solid]

3. But we have *orbitals* not *states*! Two spin-orbitals per orbital.

   Antisymmetrization.
   Lowest band: all spins paired. G = 0 (exchange integral). No contribution from G term.
   $e^- – e^-$ repulsion raises overall E above that of the single-electronic ground state of each atom
   Therefore, the work function of the solid is less than that of the single-atom ionization potential.

4. How many e^- does each atom contribute to ψ?

   alkali: $1e^- \rightarrow$ *half full* band
   alkaline earth: $2e^- \rightarrow$ *full* band

5. $\Psi(x,t)$: Motion
   phase velocity
   group velocity

6. Effective Mass

Now take a closer look at $\phi_k(x)$

$$\varphi(x) = \langle x \mid \varphi_k \rangle = \sum_{q=-\infty}^{+\infty} e^{ikq\ell} \underbrace{\langle x \mid \nu_k \rangle}_{\nu_q(x)}$$

$$\nu_q(x) = \nu_0(x - q\ell)$$ shift x by $-q\ell$ to get from site q to site 0

$$\varphi_k(x) = \sum_q e^{ikq\ell} \nu_0(x - q\ell)$$

This makes it easy to see the effect of translation of the entire ϕ by ℓ (one lattice spacing)

$$\varphi_k(x+\ell) = \sum_q e^{ikq\ell} \nu_0(\overbrace{x - q\ell + \ell}^{-\ell(q-1)})$$

take factor $e^{ik\ell}$ out of summation:

$$= e^{ik\ell} \sum_{q=-\infty}^{\infty} e^{ik(q-1)\ell} \nu_0(x - (q-1)\ell)$$

re-index infinite summation (replace $q - 1$ by q everywhere)

$$\varphi_k(x+\ell) = e^{ik\ell} \sum_q e^{ikq\ell} \nu_0(x - q\ell) = \underbrace{e^{ik\ell}}_{\text{translation of plane wave by } \ell} \varphi_k(x)$$

This implies that it is possible to write $\phi_k(x)$ in a more general form:

$$\boxed{\phi_k(x) = e^{ikx} u_k(x)}$$ **Bloch wave function**

where $u_k(x + \ell) = u_k(x)$ perodicity of ℓ

e^{ikx} expresses translational symmetry of plane wave with wavevector k
$u_k(x)$ expresses translational symmetry of lattice with spacing ℓ

<u>Now consider a localized time-dependent state</u>: "wavepacket"
We are gong to build intuitive insight by comparison to free particle.

Recall free particle:

$$\Psi(x,t) = (2\pi)^{-1/2} \int dk \underbrace{g(k)}_{\substack{\text{envelope}\\ \text{of } k\\ \text{centered}\\ \text{at } k_0}} e^{i[kx - \underbrace{E(k)t/\hbar}_{\omega t}]}$$

Group velocity: motion of *stationary phase point* (we want it to be stationary with respect to k near k_0)

$$0 = \frac{d}{dk}\left[kx - Et/\hbar\right]\Big|_{k=k_0}$$

$$x_{\text{center}}(t) = \left.\frac{dE}{dk}\right|_{k_0} t/\hbar \quad \text{position} \qquad \text{now take } \frac{d}{dt}$$

$$v_{center} = \left.\frac{dE}{dk}\right|_{k_0} \frac{1}{\hbar} \quad \text{velocity}$$

$$E = \frac{\hbar^2 k^2}{2m} \qquad \left[\frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}\right]$$

$$\left.\frac{dE}{dk}\right|_{k_0} = \frac{\hbar^2 k_0}{m}$$

$$v_{center} = v_G = \frac{1}{\hbar}\left[\left.\frac{dE}{dk}\right|_{k_0}\right] = \frac{\hbar k_0}{m}$$

group velocity

free particle relationship between! v_G and ` k and m

use this to understand motion in a periodic lattice

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Up to here we have been considering a free particle.

For 1–D lattice: the time-dependent wave function is

$$\left|\Psi(t)\right\rangle = (2\pi)^{-1/2} \int dk \underbrace{g(k)}_{\substack{\text{maximum} \\ \text{amplitude at } k_0}} e^{-iE(k)t/\hbar} \left|\varphi_k\right\rangle.$$

Instead of asking for the location of the stationary phase point, we now ask for the time dependent overlap of $\Psi(t)$ with a specific lattice site, $|\nu_q\rangle$.

$$\left\langle \nu_q \middle| \Psi(t)\right\rangle = (2\pi)^{-1/2} \int dk\, g(k) e^{i\left[kq\ell - E(k)t/\hbar\right]}$$

because $\left|\varphi_k\right\rangle = \sum_{q=-\infty}^{\infty} e^{ikq\ell} \left|\nu_q\right\rangle$

$$\left(\text{same thing as } \phi_k(x) = \sum_{q=-\infty}^{\infty} e^{ikq\ell} \left\langle x \,|\, \nu_q \right\rangle\right)$$

We can use either *state vector* or *wavefunction* picture.

and $\left\langle \nu_q \right|$ picks out only the $e^{ikq\ell}$ term from the sum over q,

because $\left\langle \nu_p \middle| \nu_q \right\rangle = \delta_{p,q}$.

Recall that $x = q\ell$, so we can think of $\left\langle \nu_q \middle| \Psi(t)\right\rangle$ as function of x,t.

We want the overlap of $\Psi(t)$ with a particular lattice site, $\left|\nu_q\right\rangle$.

$\Psi(t)$ moves and sequentially overlaps successive lattice sites.

meaningful only for regions of x near $q\ell$

$$\left\langle \nu_q \middle| \Psi(t)\right\rangle = \chi(x,t) = (2\pi)^{-1/2} \int dk \underbrace{g(k)}_{\text{real part}} \underbrace{e^{i\left[kx - E(k)t/\hbar\right]}}_{\text{phase factor}}$$

Now ask for the stationary phase factor (near $x = 0, \pm\ell, \pm 2\ell, \ldots$) with respect to k:

$$0=\frac{d}{dk}\left[kx-E(k)t/\hbar\right]$$ center of wavepacket, x_c

$$x_c(t)=\left.\frac{dE}{dk}\right|_{k_0} t/\hbar$$ wavepacket is created at $t = 0$ centered at $k = k_0$

$$v_G=\frac{dx_c}{dt}=\left.\frac{dE}{dk}\right|_{k_0}\frac{1}{\hbar}$$ This is the velocity of center of wavepacket. Up to this point, everything is identical for free particle and motion in a periodic lattice.

$$E(k)=E_0-2A\cos k\ell$$ Now use the $E\leftrightarrow k$ relationship derived for periodic (tight binding) lattice.

$$\left.\frac{dE}{dk}\right|_{k_0}=2A\ell\sin k_0\ell$$

$$v_G=\frac{2A\ell}{\hbar}\sin k_0\ell$$ This is quite different from the free particle plane wave result: $v_G=\frac{\hbar k_0}{m}$

Note that, when k_0 is at the bottom ($k = 0$, $E = E_0 - 2A$) or top ($k_0 = \pm\pi/\ell$, $E = E_0 + 2A$) of the band, $v_G = 0$.

Building of new intuition:

* $v_G \propto A$ as |A| (the adjacent site interaction) increases, it becomes easier to take a step and the wavepacket moves faster.

* $v_G \propto \ell$ (but A $\downarrow$ as $\ell \uparrow$)

because the tunneling rate decreases as ℓ increases but if A is kept constant as ℓ increases, each step is longer so velocity will be faster

* $v_G = 0$ when $k_0 = 0$ and when $k_0 = \pm\pi / \ell$

minimum E of band — **Not a surprise** because expect $k = 0 \to v = 0$

maximum E of band — **Big surprise**. Use concept of "**effective mass**" to rationalize.

e^- cannot move if it is too close to either edge of the band

"**Effective Mass**:" free vs. lattice

$$v_G = \frac{\hbar k_0}{m} \qquad v_G = \frac{2A\ell \sin k_0\ell}{\hbar} \approx \hbar k_0 \left[\frac{2A\ell^2}{\hbar^2}\right]$$

because at small $k_0\ell$

$\sin k_0\ell \approx k_0\ell$

Compare the terms and identify the reciprocal of the coefficient of ` k_0 as the "effective mass", *by analogy with the free particle*:

$$m_{\text{eff}} = \frac{\hbar^2}{2A\ell^2} \text{ at small } k_0\ell$$

* large interaction strength makes m_{eff} small
* large ℓ makes m_{eff} small (large jumps become possible)

Next: How do we show that m_{eff} increases to ∞ at the k-edges of the band ($k = \pm\pi / \ell$)?

updated August 27, 2020 @ 1:45 PM

When k_0 is near $\pm\pi/\ell$

$$k_0 = \pm\left(\frac{\pi}{\ell} - \varepsilon\right) \quad \varepsilon \text{ is small}$$

$$\sin k_0\ell = \sin\left[\pm\left(\frac{\pi}{\ell} - \varepsilon\right)\ell\right] \approx \pm\varepsilon\ell$$

$$v_G = \hbar k_0\left[\frac{2A\ell}{\hbar^2 k_0}\sin k_0\ell\right] \approx \pm\hbar k_0 \underbrace{\left[\frac{2A\ell}{\hbar^2 k_0}\varepsilon\ell\right]}_{1/m_{eff}} \qquad [v = p/m]$$

$$m_{eff} = \frac{\hbar^2 k_0}{2A\ell^2\varepsilon} \longrightarrow \infty \text{ as } \varepsilon \to 0$$

This means that at the energy of the top of a filled band: no e^- transport is possible!

1/2-Full band: $m_{eff} = \frac{\sqrt{2}}{2}\frac{\hbar^2}{A\ell^2}$ $\left(\text{slightly heavier than at bottom of band, } m_{eff} = \frac{\hbar^2}{2A\ell^2}\right)$

$k = \pm\frac{\pi}{2\ell}$ $\qquad\qquad$ $k_0 = 0$

Alternative approach to m_{eff}:

$E = p^2/2m$ for free particle

$$\left(\frac{d^2E}{dp^2}\right)^{-1} = m \quad \text{use this to define } m_{eff}$$

$$E(k) = E_0 - 2A\cos k\ell$$

$$E(p) = E_0 - 2A\cos(p\ell/\hbar)$$

$$\frac{d^2E}{dp^2} = \left(2A\ell^2/\hbar^2\right)\cos k\ell \qquad \cos k\ell = 1 - \tfrac{1}{2}(k\ell)^2 + \ldots$$

thus, at small $k\ell$ $\qquad m_{eff} = \frac{\hbar^2}{2A\ell^2}$

We have an intuitive picture for the time-evolution of a localized wavepacket. The concept of effective mass guides our intuition.

$$v_G = \frac{\hbar k}{m_{\text{eff}}}$$

$$m_{\text{eff}} = \frac{\hbar^2}{2A\ell^2} \quad \text{at bottom of band}$$

$$m_{\text{eff}} = \frac{\hbar^2 k_0}{2A\ell^2 \varepsilon} \rightarrow \infty \text{ near top of band (full band)}$$