

Solution to Homework #4.

(1)

1) Diatomic Molecule: on sites E_A, E_B hopping t } $H = \begin{bmatrix} E_A & t \\ t & E_B \end{bmatrix}$

eigenvalues are $E_{\pm} = \frac{E_A + E_B}{2} \pm \sqrt{t^2 + \left(\frac{E_B - E_A}{2}\right)^2} = \bar{E} \pm \sqrt{t^2 + \Delta^2}$

Let $\Delta = \frac{E_B - E_A}{2}$, $x = \frac{t}{\Delta}$ ($t < 0 \Rightarrow x < 0$)

if $|\varphi_A\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|\varphi_B\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ & $|\psi_+\rangle = \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix}$
 $|\psi_-\rangle = \begin{pmatrix} -\sin\theta \\ \cos\theta \end{pmatrix}$

So that both eigenstates are normalized and mutually orthogonal, then we only have to find the angle θ that takes us from (φ_A, φ_B) to (ψ_+, ψ_-)

$(H - E_{\pm})|\psi_{\pm}\rangle = (E_A - E_{\pm})\cos\theta + t\sin\theta = 0 \Rightarrow \tan\theta = -\frac{(E_A - E_{\pm})}{t} = \frac{\Delta + \sqrt{t^2 + \Delta^2}}{t}$

$\tan\theta = \frac{1 + \sqrt{1 + x^2}}{x}$; ~~But $\tan\theta = \frac{1 - \sqrt{1 + x^2}}{x}$~~ (for $x \neq 0$)

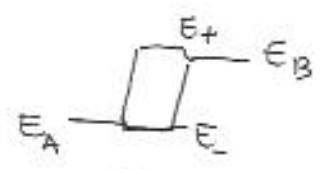
so that $x \tan\theta - 1 = \sqrt{1 + x^2} \Rightarrow x^2 \tan^2\theta + 1 - 2x \tan\theta = 1 + x^2$

Solving for x we obtain $x^2(\tan^2\theta - 1) - 2x \tan\theta = 0 \Rightarrow (x=0 \text{ or}) x = \frac{2 \tan\theta}{\tan^2\theta - 1}$
 $x = \frac{2 \tan\theta}{\tan^2\theta - 1} = -\tan 2\theta$ ↓
unacceptable

So if we let $\tan 2\theta = -x = -\frac{t}{\Delta} = \frac{|E|}{\Delta}$ we can easily express the eigenstates in terms of θ .

$x \rightarrow 0^-$ $\theta \rightarrow \frac{\pi}{2}^+$ $|\psi_+\rangle \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ $|\psi_-\rangle \rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\varphi_A\rangle$ we are in the ionic limit as $t \ll \Delta = \frac{E_B - E_A}{2}$

$|\psi_-\rangle$ is of lower energy and therefore the bonding state.



$|\psi_-\rangle \cong |\varphi_A\rangle$ is the correct answer since $E_A \sim E_-$ ($\theta = \frac{\pi}{2}^+$ is correct)

$$\theta = \frac{\pi}{2}^+ \text{ being correct } |\psi_+\rangle = \begin{pmatrix} -\sin\theta \\ \cos\theta \end{pmatrix} \sim \begin{pmatrix} -1 \\ 0 \end{pmatrix}$$

$$\begin{aligned} \sin\theta &\sim 1 \\ \cos\theta &\sim \frac{x}{2} \end{aligned}$$

$$\text{or } -\sin\theta |\psi_A\rangle + \cos\theta |\psi_B\rangle$$

$$\text{or } \sin\theta |\psi_A\rangle \approx \cos\theta |\psi_B\rangle$$

$$\begin{aligned} |\psi_-\rangle &\sim |\psi_A\rangle + \left| \frac{2t}{2\Delta} \right| |\psi_B\rangle \\ &= |\psi_A\rangle + \frac{t}{2\Delta} |\psi_B\rangle \end{aligned}$$

which can also be verified by using perturbation theory ($t =$ off diagonal elt used as perturbation)

$$P_A = |\langle \psi_A | \psi_- \rangle|^2 \approx 1 \quad P_B = |\langle \psi_B | \psi_- \rangle|^2 \sim \frac{4t^2}{4\Delta^2} \text{ is very small.}$$

The bonding e^- is mostly on the A atom with the lowest onsite energy.

• $X \rightarrow -\infty$ $\Delta E \ll (t) \rightarrow$ covalent limit

$$\tan\theta = 1 \rightarrow \theta = \frac{\pi}{4} \left[\frac{3\pi}{4} \right]$$

physically correct

$$|\psi_+\rangle \rightarrow \frac{1}{\sqrt{2}} (|\psi_A\rangle - |\psi_B\rangle)$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} (|\psi_A\rangle + |\psi_B\rangle)$$

(+) is needed

for the bonding state

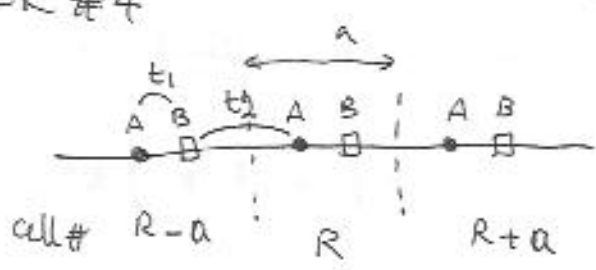
$$P_A = |\langle \psi_A | \psi_- \rangle|^2 = \frac{1}{2}$$

$$P_B = |\langle \psi_B | \psi_- \rangle|^2 = \frac{1}{2}$$

} the e^- is equally shared between the 2 atoms.

Solution to HOMEWORK #4

(3)



Block Basis : $|\varphi_k^A\rangle = \sum_R \frac{e^{ikR}}{\sqrt{N}} |\varphi_R^A\rangle$.

$$\langle \varphi_k^A | H | \varphi_{k'}^A \rangle = \sum_{RR'} \frac{1}{N} e^{-ikR} e^{ik'R'} \langle \varphi_R^A | H | \varphi_{R'}^A \rangle$$

But there is no hopping between A-A neighbors $\Rightarrow \langle \varphi_R^A | H | \varphi_{R'}^A \rangle = E_A \delta_{RR'}$

$$\Rightarrow \langle \varphi_k^A | H | \varphi_{k'}^A \rangle = \left[\sum_R \frac{1}{N} e^{i(k'-k)R} \right] E_A = E_A \delta_{k,k'}$$

same for $\langle \varphi_k^B | H | \varphi_{k'}^B \rangle = E_B \delta_{k,k'}$

$$\langle \varphi_k^A | H | \varphi_{k'}^B \rangle = \sum_{RR'} \frac{1}{N} e^{-ikR} e^{ik'R'} \langle \varphi_R^A | H | \varphi_{R'}^B \rangle$$

$$= \sum_R \frac{1}{N} e^{i(k'-k)R} \left[\delta_{R,R'} t_1 + \delta_{R',R-a} t_2 \right]$$

$$= \delta_{k,k'} (t_1 + t_2 e^{-ika})$$

likewise $\langle \varphi_k^B | H | \varphi_{k'}^A \rangle = \delta_{k,k'} (t_1 + t_2 e^{+ika})$

As expected, from Bloch's theorem, k-states are only coupled to k-states and we always have, due to periodicity, $\langle k' | H | k \rangle \propto \delta_{kk'}$

$$H(k) = \begin{bmatrix} E_A & t_1 + t_2 e^{-ika} \\ t_1 + t_2 e^{ika} & E_B \end{bmatrix} \quad \text{Det}(H - \lambda I) = 0 \Rightarrow$$

$$(E_A - \lambda)(E_B - \lambda) = |t_1 + t_2 e^{ika}|^2 = t_1^2 + t_2^2 + 2t_1 t_2 \cos ka$$

$$\lambda^2 - (E_A + E_B)\lambda + E_A E_B - |t_1 + t_2 e^{ika}|^2 = 0$$

$$\lambda = \frac{E_A + E_B}{2} \pm \sqrt{\underbrace{\left(\frac{E_A + E_B}{2}\right)^2 - E_A E_B}_{\left(\frac{E_A - E_B}{2}\right)^2} + T^2}$$

with $T^2 = t_1^2 + t_2^2 + 2t_1 t_2 \cos ka$

1) Covalent limit ($E_A = E_B$) ; monoatomic chain ($t_1 = t_2$)

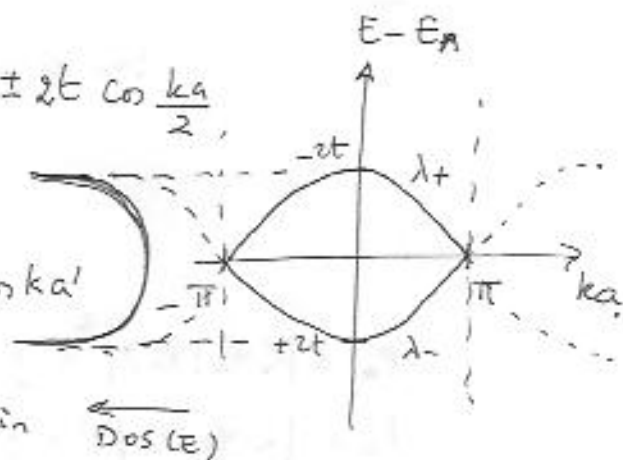
$$\lambda_{\pm} = E_A \mp t \sqrt{2 + 2 \cos ka} = E_0 \pm 2t \cos \frac{ka}{2}$$

this is the folded dispersion

relation of the monoatomic chain $E_0 + 2t \cos ka'$

with $a' = \frac{a}{2}$ being the lattice

constant of the monoatomic chain



2) Covalent limit ($E_A = E_B$) ; diatomic chain $t_1 = 2t_2 = 2t$

$$T^2 = 4t^2 + t^2 + 4t^2 \cos ka$$

$$\lambda_{\pm} = E_A \pm \sqrt{5t^2 + 4t^2 \cos ka}$$

$$\lambda_{\pm}(k=0) = E_A \pm \sqrt{5t^2 + 4t^2} = E_A \pm 3t$$

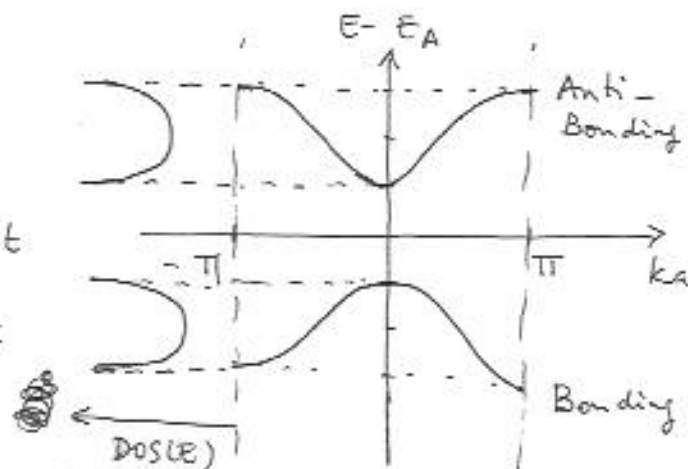
$$\lambda_{\pm}(k=\frac{\pi}{a}) = E_A \pm \sqrt{5t^2 - 4t^2} = E_A \pm t$$

The lower band is the bonding

state of the dimer weighted by e^{ikR} in cell R

and the higher band is the antibonding superposition

state weighted by e^{ikR} in cell R



3) Ionic limit ($E_A = 0$; $E_B = 2t$) $t_1 = t_2 = t$.

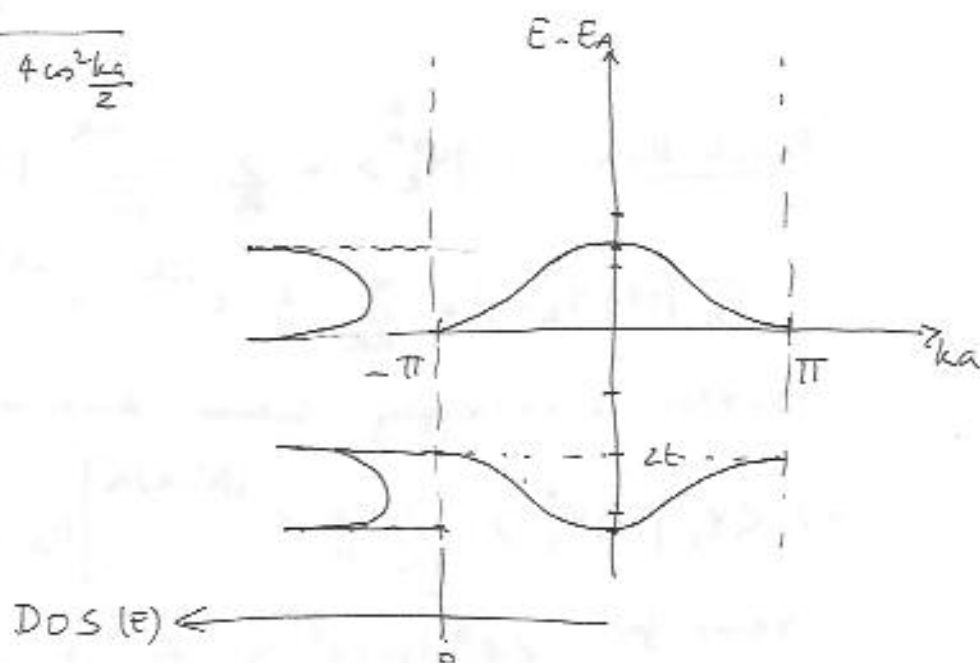
$$\lambda_{\pm} = t \pm \sqrt{t^2 + T^2}$$

$$= t \pm t \sqrt{1 + 4 \cos^2 \frac{ka}{2}}$$

$$T^2 = 2t^2 (1 + \cos ka) = 4t^2 \cos^2 \frac{ka}{2}$$

$$\lambda_{\pm}(k=0) = t \pm t \sqrt{5}$$

$$\lambda_{\pm}(k=\frac{\pi}{a}) = t \pm t$$



At the top or bottom of every band, the dispersion is quadratic, leading in 1D to a $1/\sqrt{E-E}$ singularity edge

for example in case 1. $E = E_0 + 2t \cos \frac{ka}{2}$

$$\text{DOS}(E) dE = \underbrace{2}_{(k \& -k)} \times \underbrace{\frac{L}{2\pi}}_{\text{dos}(k)} \times dk$$

$$\frac{dE}{dk} = -2t \frac{a}{2} \sin \frac{ka}{2} = -ta \sin \frac{ka}{2}$$

$$\Rightarrow \text{DOS}(E) = \frac{L}{\pi} \left| \frac{dk}{dE} \right| = \frac{L}{\pi} \frac{1}{|ta \sin \frac{ka}{2}|} = \frac{L}{\pi} \frac{1}{|ta|} \frac{1}{\sqrt{4 - \left(\frac{E - E_0}{2t}\right)^2}}$$

$$= \frac{2L}{a\pi} \frac{1}{\sqrt{4t^2 - (E - E_0)^2}} = \frac{2N}{\pi} \frac{1}{\sqrt{4t^2 - (E - E_0)^2}}$$