* tight-binding picture

→ use as a local basis a collection of atomic orbitals

$$\phi_\alpha(\vec{r} - \vec{R}_i - \vec{\tau}_i)$$

α: orbital type; $\vec{R}_i$: Bravais lattice vector; i: site index; $\vec{\tau}_i$: basis vector

→ orbitals are spatially confined and have no overlap with plane waves

→ for convenience, orbitals are generally chosen to be orthogonal onsite (like hydrogenic wavefunctions)

→ otherwise, overlaps are of the form

$$\langle \phi_{i\alpha} | \phi_{j\beta} \rangle = \delta_{ij}\delta_{\alpha\beta} + (1-\delta_{ij}) S_{i\alpha;j\beta}$$

→ energetics determined by kinetic energy matrix elements

$$-t_{i\alpha;j\beta} = \langle \phi_{i\alpha} | \hat{H}_0 | \phi_{j\beta} \rangle$$

$$= \int d^3r\, \phi^*_\alpha(\vec{r} - \vec{R}_i - \vec{\tau}_i) \left[-\frac{\hbar^2 \nabla^2}{2m} \right] \phi_\beta(\vec{r} - \vec{R}_j - \vec{\tau}_j)$$

→ single-particle wavefunctions of the form

$$\psi(\vec{r}) = \sum_{i,\alpha} \psi_{i\alpha}\, \phi_\alpha(\vec{r}-\vec{R}_i-\vec{\tau}_i)$$

satisfy a <u>generalized</u> eigenvalue equation

$$\sum_{j,\beta} (-t_{i\alpha;j\beta})\,\psi_{j\beta} = E \sum_{j,\beta} S_{i\alpha;j\beta}\,\psi_{j\beta}$$

* for an arbitrary system of N atoms with n_0 local orbitals, the problem involves an $Nn_0 \times Nn_0$ matrix (and the dimension is $\sum_{i=1}^{N} n_{0,i}$ if the number of local orbitals varies from site to site).

* take advantage of translational symmetry in a regular crystal

→ build states of definite wavevector $\vec{k}$:

$$|\phi_{\vec{k},\tau,\alpha}\rangle = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\, |\phi_{\vec{R},\vec{\tau},\alpha}\rangle$$

$$|\phi_{\vec{R},\vec{\tau},\alpha}\rangle = \frac{1}{N_u}\sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}}\, |\phi_{\vec{k},\vec{\tau},\alpha}\rangle$$

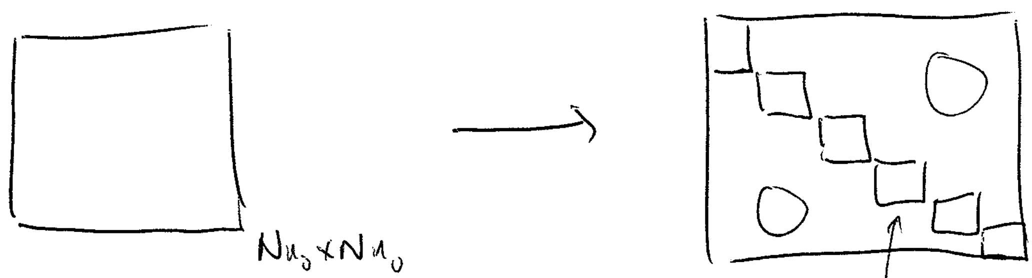
N_u = # unitcells = N/n_b

N: # atoms; n_b: size of basis

$\rightarrow$ this block diagonalizes the problem in $\vec{k}$-space

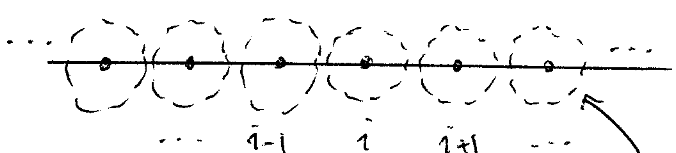
$$\langle \phi_{\vec{k},\vec{\tau},\alpha} | \hat{O} | \phi_{\vec{k}',\vec{\tau}',\beta} \rangle \xrightarrow{\text{F.T.}} \delta_{\vec{k}\vec{k}'} \langle \phi_{\vec{k},\vec{\tau},\alpha} | \hat{O} | \phi_{\vec{k},\vec{\tau}',\beta} \rangle$$

any trans. inv. operator



$$\frac{N n_o}{N_u} = \frac{N n_o}{N/n_b} = n_o n_b$$

<u>EXAMPLE</u>: one species linear chain



single s-orbital $\phi_s(\vec{r}) \sim e^{-a\vec{r}^{\,i}}$ centred on each site

$n_o = n_b = 1$

$\Rightarrow$ trivial 1×1 matrix structure "hopping" elements

$-t_{i,i} \equiv -t_0$

$-t_{i,i+1} \equiv -t_1$

$-t_{i,i+2} \equiv -t_2$

$\vdots$

overlaps

$S_{i,i} = 1$

$S_{i,i+1} \equiv S_1$

$S_{i,i+2} \equiv S_2$

$\vdots$

$\rightarrow$ we expect t_{ij} and s_{ij} to fall off exponentially in the distance $|i-j|$

$$\langle \phi_k | \hat{H}_0 | \phi_k \rangle = \sum_{j=-\infty}^{\infty} e^{ikaj} \left[(-t_0)\delta_{j,0} + (-t_1)(\delta_{j,1} + \delta_{j,-1}) + \cdots \right]$$

$$= -t_0 - 2t_1 \cos ka - 2t_2 \cos 2ka - \cdots$$

(truncated at some distance)

$$\langle \phi_k | \phi_k \rangle = \sum_{j=-\infty}^{\infty} e^{ikaj} \left(\delta_{j,0} + s_1(\delta_{j,1} + \delta_{j,-1}) + \cdots \right)$$

$$= 1 + 2s_1 \cos ka + 2s_2 \cos 2ka + \cdots$$

→ solve $\langle \phi_k | \hat{H}_0 | \phi_k \rangle = \varepsilon_k \langle \phi_k | \phi_k \rangle$ to get

$$\varepsilon_k = \frac{-t_0 - 2t_1 \cos ka - 2t_2 \cos 2ka - \cdots}{1 + 2s_1 \cos ka + 2s_2 \cos 2ka + \cdots}$$

$$= -t_0 - 2(t_1 - t_0 s_1)\cos ka + \cdots$$

$$= -t_0 - 2(t_1 - t_0 s_1)\left(1 - \tfrac{1}{2}k^2a^2 + \cdots\right) + \cdots$$

$$= -\left[t_0 + 2(t_1 - t_0 s_1) + \cdots\right] + \left[(t_1 - t_0 s_1)a^2 + \cdots\right]k^2$$

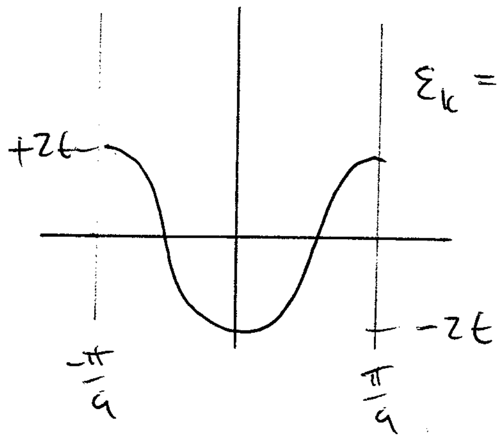
$$\equiv \text{const} + \frac{\hbar^2 k^2}{2m^*}$$

→ parabolic band near $k=0$ with effective mass

$$m^* = \frac{\hbar^2}{2\left[(t_1 - t_0 s_1)a^2 + \cdots\right]}$$

well-defined scalar near the bottom of the band

* typical "single-band" approximation



$\varepsilon_k = -2t\cos ka$

→ particle-hole symmetric under $k \to \frac{\pi}{a} - k$

→ locally quadratic at $k=0$ and $k = \pm\frac{\pi}{a}$

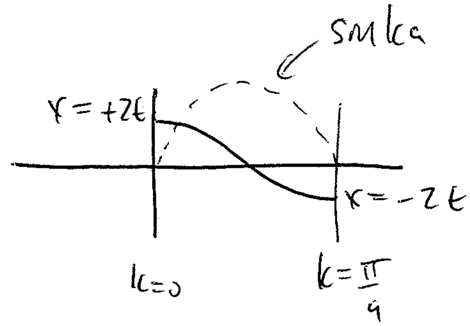
→ corresponding DOS

$$D(\omega) = \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{dk}{2\pi}\,\delta(\omega - \varepsilon_k) = \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{dk}{2\pi}\,\delta(\omega + 2t\cos ka)$$

$$= \frac{1}{\pi}\int_0^{\frac{\pi}{a}} dk\,\delta(\omega + 2t\cos ka)$$

let $x = 2t\cos ka$

$dx = -2ta\sin ka \cdot dk$



$$\Rightarrow dk = \frac{-1}{2ta}\frac{dx}{\sin ka} = -\frac{1}{2ta}\frac{dx}{\sqrt{1-\cos^2 ka}}$$

$$= -\frac{1}{2ta}\frac{dx}{\sqrt{1-\left(\frac{x}{2t}\right)^2}} = -\frac{1}{a}\frac{dx}{\sqrt{4t^2 - x^2}}$$

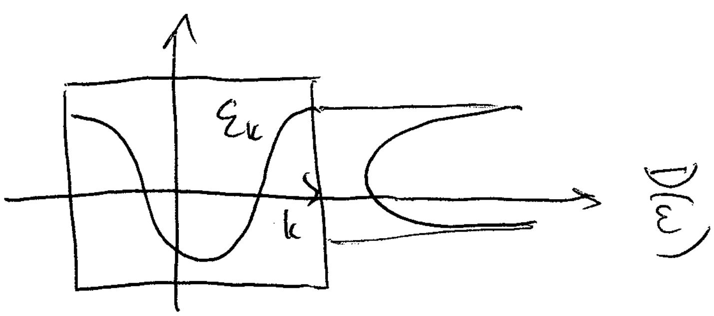
$$D(\omega) = -\frac{1}{\pi a}\int_{+2t}^{-2t} dx \; \frac{\delta(\omega - x)}{\sqrt{4t^2 - x^2}} = \frac{1}{\pi a}\,\frac{\theta(4t^2-\omega^2)}{\sqrt{(2t-\omega)(2t+\omega)}}$$

Heaviside function to account for poles lying within the range of integration

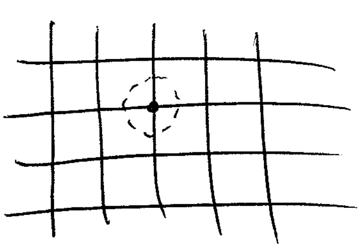
→ singularities near the band edges:

$$D(-2t+\varepsilon) = D(2t-\varepsilon) \sim \frac{\theta(\varepsilon)}{\pi a\sqrt{4t\,\varepsilon}}$$

$1/\sqrt{\varepsilon}$ characteristic of one-dimensional behavior



ANOTHER EXAMPLE: one-species square lattice



$$\langle \phi_k | \hat{H}_0 | \phi_k \rangle = -t_0 - 2t_1(\cos k_x a + \cos k_y a) + \cdots$$

$$\langle \phi_k | \phi_k \rangle = 1 + 2s_1(\cos k_x a + \cos k_y a) + \cdots$$

$$\varepsilon_k = \frac{\langle \phi_k | \hat{H}_0 | \phi_k \rangle}{\langle \phi_k | \phi_k \rangle} = \text{const} - 2t(\cos k_x a + \cos k_y a)$$

→ near the bottom of the band

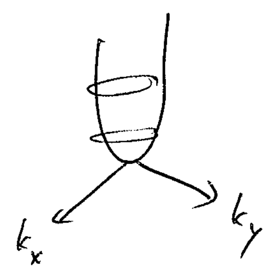
$$\varepsilon_k = -2t\left[1 - \frac{1}{2}(k_x a)^2 + \frac{1}{24}(k_x a)^4 + \dots\right.$$
$$\left. + 1 - \frac{1}{2}(k_y a)^2 + \frac{1}{24}(k_x a)^4 + \dots\right]$$

$$= -4t + ta^2(k_x^2 + k_y^2) - \frac{ta^4}{12}(k_x^4 + k_y^4)$$

$$= -4t + ta^2|\vec{k}|^2 - \frac{ta^4}{12}|\vec{k}|^4(\cos^4\theta + \sin^4\theta)$$

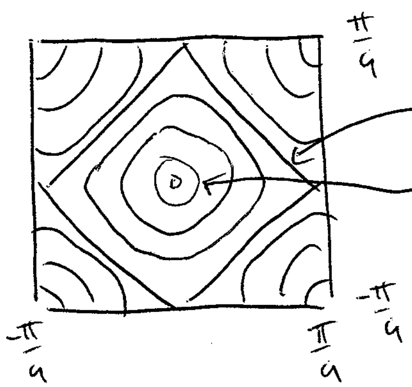
quadratic with mass $m = \frac{\hbar^2}{2ta^2}$

anisotropy with $k_x = |\vec{k}|\cos\theta$, $k_y = |\vec{k}|\sin\theta$



→ level surfaces deviate from circular near the centre of the band (in energy space; i.e. half-filling)

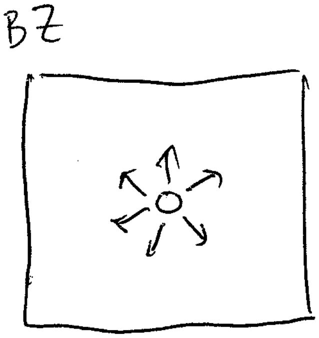
BZ



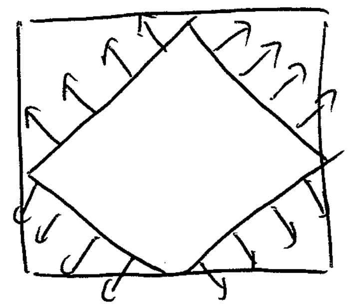
$|k_x| + |k_y| = \frac{\pi}{a}$ (diamond)

$k_x^2 + k_y^2 \simeq$ const (circle)

→ unusual consequences: recall that group velocity $\vec{v} = \vec{\nabla}\varepsilon_k$ is normal to the level surfaces



free electron-like



only four allowed directions of propagation

→ effective mass has an increasingly tensorial character away from the bottom of the band

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$\nabla\varepsilon_k = \frac{\hbar^2 \vec{k}}{m} = 2ta^2\vec{k}$$

$$\left(\frac{1}{m^*}\right)_{\alpha\beta} = \hbar^{-2}\frac{\partial^2\varepsilon_k}{\partial k_\alpha \partial k_\beta}$$

$$= \frac{\hbar^2}{2ta^2}\delta_{\alpha\beta}$$

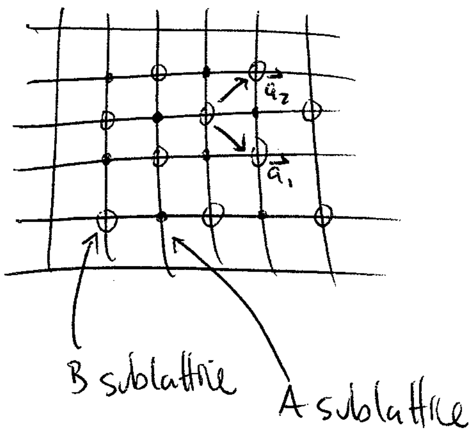
$$\nabla\varepsilon_k = \pm\hat{e}_x \pm \hat{e}_y$$

$$(\nabla\varepsilon_k)_\alpha = \hbar^2\left(\frac{1}{m^*}\right)_{\alpha\beta} k_\beta$$

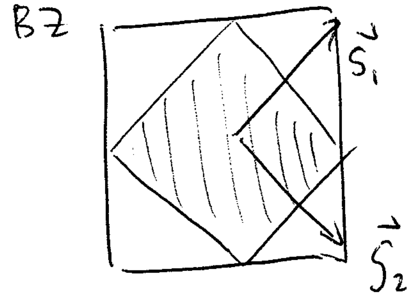
average value over the FS

$$\frac{1}{m^*} = \int_{BZ} d^2k \, \frac{\partial^2\varepsilon_k}{\partial k_\alpha \partial k_\beta}\,\delta(\varepsilon_k - \varepsilon_F)$$

YET ANOTHER EXAMPLE: two-species square lattice



$$\vec{a}_{1,2} = a\,(\hat{e}_x \pm \hat{e}_y); \quad \vec{g}_{1,2} = \frac{\pi}{a}(\hat{e}_x \pm \hat{e}_y)$$



onsite energy levels

$$-t_0^A \equiv \varepsilon^A, \quad -t_0^B \equiv \varepsilon^B$$

inter-sublattice hopping and overlaps

$$-t_1^{AB} \text{ and } s_1^{AB}$$

$2\cos k_x a$ $\quad$ $2\cos k_y a$

intra-sublattice hopping and overlaps

$$-t_2^{AA}, -t_2^{BB} \text{ and } s_2^{AA}, s_2^{BB}$$

$2\cos(k_x - k_y)a$ $\quad$ $2\cos(k_x + k_y)a$

→ 2×2 matrix of kinetic energy terms

$$\mathcal{H} = \langle \phi_{k,\vec{\tau}} | \hat{H}_0 | \phi_{k,\vec{\tau}'} \rangle = \begin{pmatrix} \varepsilon^A - 4t_2^{AA}\cos k_x a \cos k_y a & -2t_1^{AB}(\cos k_x a + \cos k_y a) \\ -2t_1^{AB}(\cos k_x a + \cos k_y a) & \varepsilon^B - 4t_2^{BB}\cos k_x a \cdot \cos k_y a \end{pmatrix}$$

→ 2×2 matrix of overlaps

$$S = \langle \phi_{\vec{k},\tau} | \phi_{\vec{k},\tau'} \rangle = \begin{pmatrix} 1 + 4 s_2^{AA} \cos k_x a \cos k_y a & 2 s_1^{AB} (\cos k_x a + \cos k_y a) \\ 2 s_1^{AB} (\cos k_x a + \cos k_y a) & 1 + 4 s_2^{BB} \cos k_x a \cos k_y a \end{pmatrix}$$

→ Solve eigenvalue problem

$$\mathcal{H} \psi = E S \psi \quad \text{or} \quad (S^{-1} \mathcal{H}) \psi = E \psi$$

here analytically ...

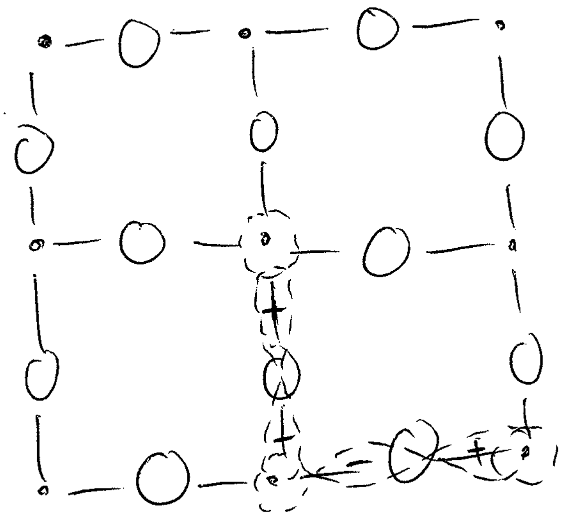
$$\mathcal{H} = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \qquad S = \begin{pmatrix} u & v \\ v & w \end{pmatrix}$$

$$E^{(\pm)} = \frac{1}{2(uw - v^2)} \Big[\big(u^2c^2 - 4ucvb - 2ucaw - 4vbaw + a^2w^2 + 4uwb^2 + 4v^2ac \big)^{1/2} \pm (uc - 2vb + aw) \Big]$$

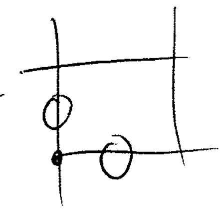
but otherwise numerically at each $\vec{k}$ point for higher-dimensional matrices

YET YET ANOTHER EXAMPLE: p-state bands

→ case in which the orbitals have directionality



unit cell with 3 element basis



assign one s-orbital to 

and one p-orbital to 

$$\mathcal{H} = \begin{pmatrix} \varepsilon^s & -2it_1 \sin k_x a & -2it_1 \sin k_y a \\ +2it_1 \sin k_x a & \varepsilon^p & 0 \\ +2it_1 \sin k_y a & 0 & \varepsilon^p \end{pmatrix}$$

$$E = \varepsilon^p, \ \frac{1}{2}\left[\varepsilon^s + \varepsilon^p \pm \sqrt{(\varepsilon^s - \varepsilon^p)^2 + 16t_1^2\left[\sin^2 k_x a + \sin^2 k_y a\right]}\right]$$