LECTURE 3: From atoms to 1D nanowires: Tight-binding Hamiltonian

1° H_2^+ molecule as example for chemical bond

$$\hat{H} = \underbrace{\frac{\hat{p}_e^2}{2m_e} + \frac{\hat{P}_1^2 + \hat{P}_2^2}{2m_p}}_{\hat{K}_{pp}} + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\vec{r}_e - \vec{R}_1|} + \frac{1}{|\vec{r}_e - \vec{R}_2|} - \underbrace{\frac{1}{|\vec{R}_1 - \vec{R}_2|}}_{\hat{V}_{pp}}\right)$$

$$\hat{H}\,\Phi(\vec{r}_e, \vec{R}_1, \vec{R}_2) = E\,\Phi(\vec{r}_e, \vec{R}_1, \vec{R}_2)$$

is 3-body problem and unlike H atom cannot be solved exactly

$$\vec{R} = \vec{R}_1 - \vec{R}_2$$

→ Born-Oppenheimer approximation using $m_p/m_e \approx 1836$:

$$\Phi(\vec{r}_e, \vec{R}_1, \vec{R}_2) = \psi_{\vec{R}_1,\vec{R}_2}(\vec{r}_e)\cdot \chi(\vec{R}_1, \vec{R}_2)$$

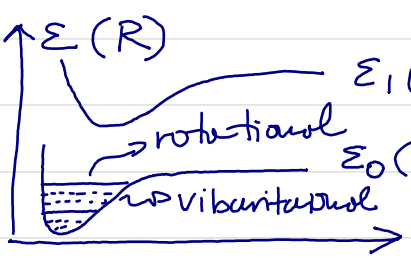
($\vec{R}_1, \vec{R}_2$: parameters rather than variable)

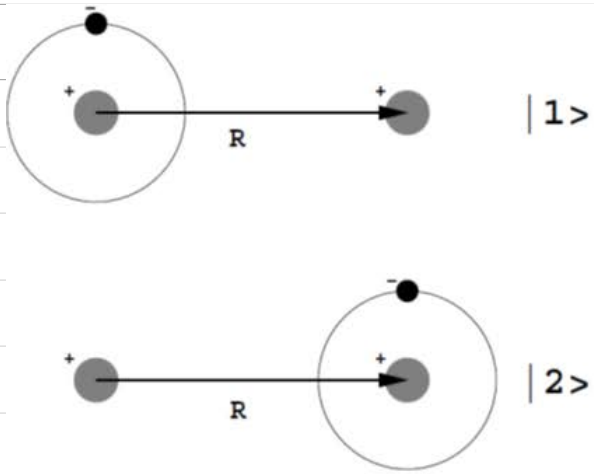
$$\hat{H}_e\,\psi(\vec{r}_e) = \mathcal{E}(\vec{R}_1, \vec{R}_2)\,\psi(\vec{r}_e)$$

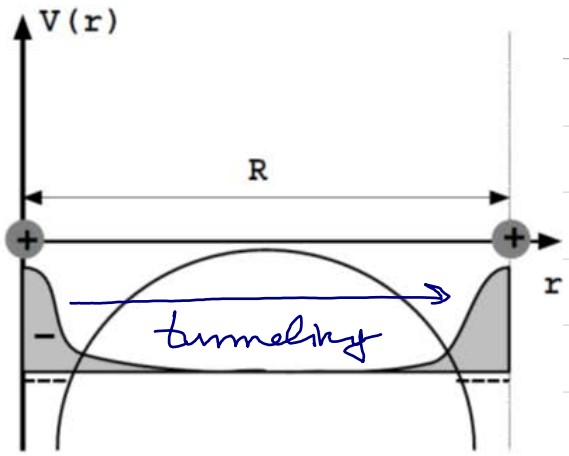
$$\underbrace{\left[\hat{K}_p + \hat{V}_{pp} + \mathcal{E}(\vec{R}_1, \vec{R}_2)\right]\chi(\vec{R}_1, \vec{R}_2) = E\,\chi(\vec{R}_1, \vec{R}_2)}$$

classical approximation: $M\frac{d^2\vec{R}_i}{dt^2} = -\frac{\partial}{\partial \vec{R}_i}\left[\hat{V}_{pp} + \mathcal{E}(\vec{R}_1, \vec{R}_2)\right]$

$\hat{V}_{pp} + \mathcal{E}(\vec{R}_1, \vec{R}_2)$ is adiabatic Born-Oppenheimer potential energy surface which determines molecule geometry, nuclei vibrational and rotational energy levels, and nuclei dynamics







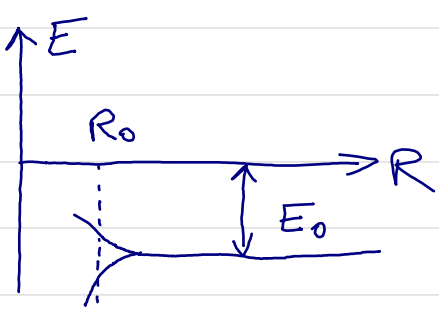
→ consider simplification which disregards all states except: $|1\rangle$ electron localized on proton 1 $|2\rangle$ electron localized on proton 2 } variational subspace

$$\langle \vec{r}|1\rangle = \Phi_S(\vec{r}-\vec{R}_1) = \frac{1}{\sqrt{\pi}\, a^{3/2}} e^{-|\vec{r}-\vec{R}_1|/a}$$

$$\langle \vec{r}|2\rangle = \Phi_S(\vec{r}-\vec{R}_2) = \frac{1}{\sqrt{\pi}\, a^{3/2}} e^{-|\vec{r}-\vec{R}_2|/a}$$

$R \to \infty \Rightarrow$ $\hat{H}_0|1\rangle = E_0|1\rangle$, $\hat{H}_0|2\rangle = E_0|2\rangle$ $\quad \langle 1|2\rangle = 0$, $\langle 1|1\rangle = \langle 2|2\rangle = 1$

$$\hat{H}_0 = E_0|1\rangle\langle 1| + E_0|2\rangle\langle 2| \quad \text{or} \quad \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix}$$ matrix representation



$R \to R_0 \Rightarrow$ electron can tunnel through the barrier

$$\hat{H}_t|1\rangle \propto t|2\rangle, \quad \hat{H}_t^2 = \hat{I}$$

t is function of R; $\hat{H}_t = -t|1\rangle\langle 2| - t|2\rangle\langle 1|$

$\hat{H} = \hat{H}_0 + \hat{H}_t$ $\quad \hat{H} \mapsto \begin{pmatrix} E_0 & -t \\ -t & E_0 \end{pmatrix}$ as matrix representation

$|1\rangle \mapsto \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$|2\rangle \mapsto \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$\hat{H}\begin{pmatrix} a \\ b \end{pmatrix} = E\begin{pmatrix} a \\ b \end{pmatrix}$

$\hat{H}|A\rangle = (E_0 + t)|A\rangle$

$\hat{H}|B\rangle = (E_0 - t)|B\rangle$

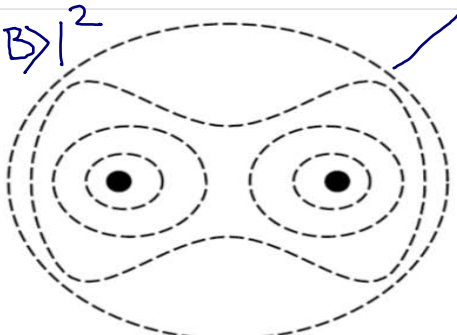
$|A\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \mapsto \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$

$|B\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \mapsto \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$

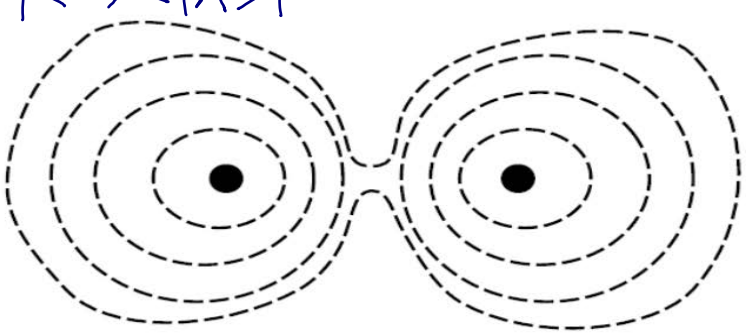
$\langle \vec{r}, \vec{R}|A\rangle = \phi_s(\vec{r}) - \phi_s(\vec{r} - \vec{R})$

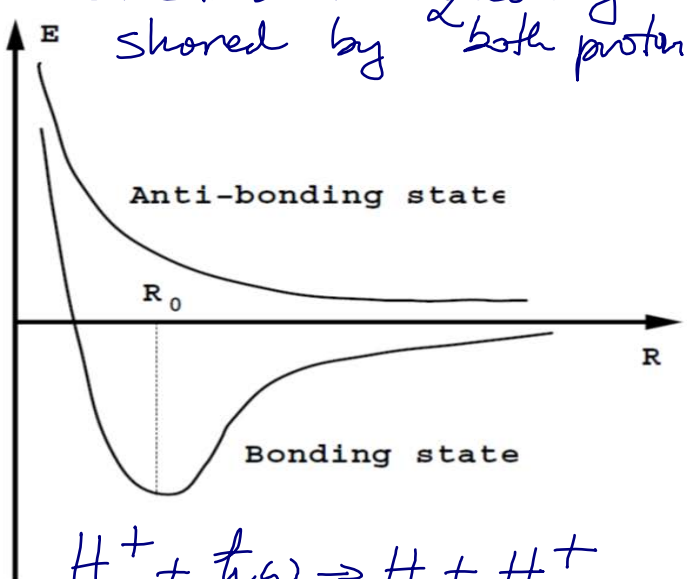
$\langle \vec{r}, \vec{R}|B\rangle = \phi_s(\vec{r}) + \phi_s(\vec{r} - \vec{R})$

$|\langle \vec{r}, \vec{R}|B\rangle|^2$ → covalent bond implies that electron is equally shared by both protons



$|\langle \vec{r}, \vec{R}|A\rangle|^2$





$H_2^+ + \hbar\omega \rightarrow H + H^+$

↑ absorb energy to go from $|B\rangle$ to $|A\rangle$

2° Band structure of one-dimensional nanowire

↳ freely suspended chain of atoms does not exist, but using substrate:

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Imaging of spin waves in atomically designed nanomagnets

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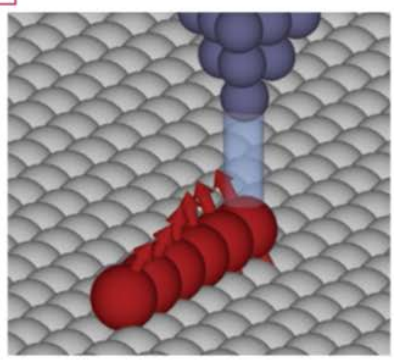
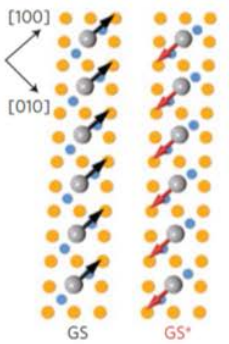
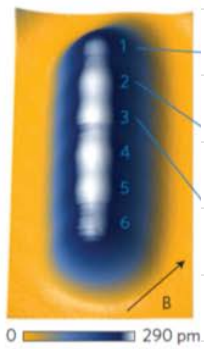
Fe atoms on Cu_2N lattice







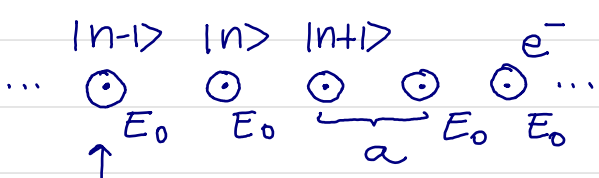
- Bravais lattice terminology for describing translational invariance

↳ primitive unit cell (PUC) contains only one lattice point

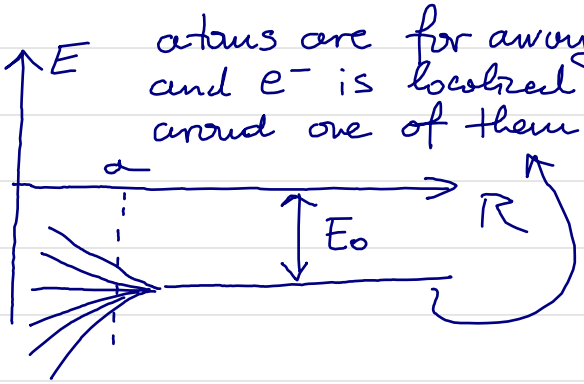
↳ Wigner-Seitz PUC

$\vec{a}$ is lattice spacing

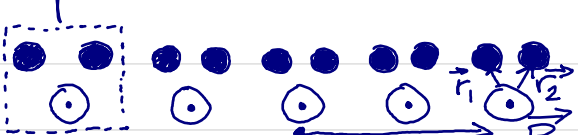
primitive lattice vectors are the shortest possible and span the whole lattice $\vec{R}_n = n \cdot \vec{a}$



one atom per unit cell with one valence orbital per atom retained



degenerate E_0 splits into N levels for N atoms or band of energy for $N \to \infty$



↳ lattice with a basis of 3 atoms

$\langle n|m\rangle = \delta_{nm}$, $\langle x|n\rangle = \phi_s(x - na)$ is s-orbital

$$\hat{H} = \sum_n \varepsilon_0 |n\rangle\langle n| - t \sum_n \left(|n\rangle\langle n+1| + |n+1\rangle\langle n| \right)$$

$$\underbrace{\hat{H}|\psi\rangle = \mathcal{E}|\psi\rangle}, \quad |\psi\rangle = \sum_{n=-\infty}^{\infty} c_n |n\rangle$$

$$\Updownarrow$$

$$\begin{pmatrix} \ddots & & & & \\ & E_0 & -t & 0 & 0 \\ & -t & E_0 & -t & 0 \\ & 0 & -t & E_0 & -t \\ & & 0 & -t & E_0 \\ & & & 0 & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ c_{n-1} \\ c_n \\ c_{n+1} \\ \vdots \end{pmatrix} = \mathcal{E} \begin{pmatrix} \vdots \\ c_{n-1} \\ c_n \\ c_{n+1} \\ \vdots \end{pmatrix}$$

matrix representation of time-independent Schrödinger equation in the basis of localized atomic orbitals $|n\rangle$ → in chemistry, solid state physics and DFT literature you will find LCAO term for this

- Eigenenergies or "band structure"

$$\underbrace{-tc_{n-1} + \varepsilon_0 c_n - tc_{n+1} = \mathcal{E} \cdot c_n}$$

this is difference equation ⇒ search for solution

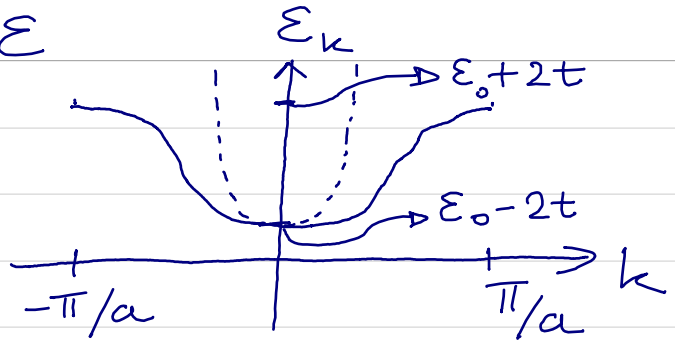
$$c_n = e^{ikna}$$

$$\underbrace{-\pi/a \leq k < \pi/a}_{\text{first Brillouin zone}}$$

$$\varepsilon_0 e^{ikna} - t\left[e^{ik(n+1)a} + e^{ik(n-1)a}\right] = \mathcal{E} e^{ikna} \quad / : e^{ikna}$$

$$\varepsilon_0 - t\left[e^{ika} + e^{-ika}\right] = \varepsilon$$

$$\varepsilon_k = \varepsilon_0 - 2t\cos ka$$



$$ka \ll 1 \Rightarrow \varepsilon_k \approx \varepsilon_0 - 2t + t k^2 a^2$$

$$\underbrace{\varepsilon_k - (E_0 - 2t) \approx \frac{\hbar^2 k^2}{2m^*}, \quad m^* = \frac{\hbar^2}{2a^2 t}}$$

parabolic energy–momentum dispersion is approximation valid only at the bottom of the band

- Eigenvectors or "Bloch states"

$|\psi_k\rangle$ is eigenvector for ε_k

$$|\psi_k\rangle = \sum_{n=-\infty}^{\infty} e^{ikna}|n\rangle \Rightarrow \underbrace{\langle x|\psi_k\rangle}_{\psi_k(x)} = \sum_{n=-\infty}^{\infty} e^{ikna}\phi_s(x-na)$$

$$\psi_k(x+a) = \sum_{n=-\infty}^{\infty} e^{ikna}\phi_0\left(x-(n-1)a\right)$$

$$= e^{ika}\cdot\sum_{n=-\infty}^{\infty} e^{ik(n-1)a}\phi_0\left(x-(n-1)a\right)$$

operator of discrete translations

$$= e^{ika}\psi_k(x), \text{ so } [\hat{H}, \hat{T}_a] = 0 \text{ but } \psi_k(x) \text{ is not periodic}$$

$\psi_k(x) = e^{ikx} u_k(x)$ where $u_k(x+a) = u_k(x)$

$\underbrace{|\psi_k(x+na)|^2 = |\psi_k(x)|^2}$

Bloch electron is delocalized over the whole lattice

- Compare Bloch electron with free electron

$\psi_k(x) \propto e^{ikx}$ for free electron

$$\psi_k(x) = e^{ikx} \sum_G \alpha_G e^{iGx}, \quad G \cdot a = 2\pi$$

$$= \sum_G \alpha_G e^{i(k+G)x}$$

↑ reciprocal lattice vector (in 1D just number)

→ Bloch wavefunction

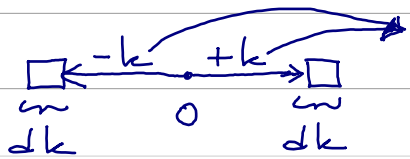
- what is $\langle \psi_k | \underbrace{\hat{p}_x}_{-i\hbar\partial/\partial x} | \psi_k \rangle$ → free electron? → Bloch electron?

- Density of states

$\varepsilon_k = -2t \cos ka$ (ε_0 defines the reference energy)

→ chain of finite length L with periodic boundary conditions

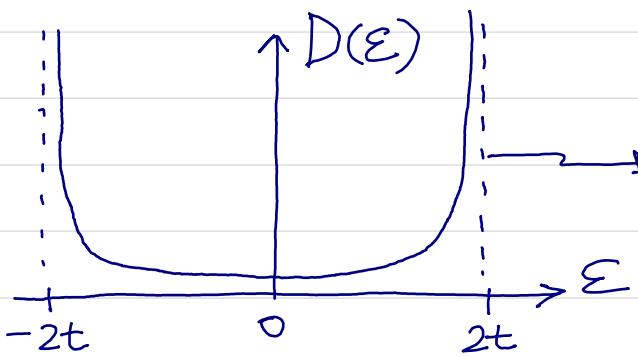
$k_n = \frac{2\pi}{L} n$, $\frac{2\pi/a}{2\pi/L} = \frac{L}{a} = N - 1 \approx N$ states



$$\frac{2\,dk}{2\pi/L} = D_0(\varepsilon)\,d\varepsilon$$

$$D(\varepsilon) = \frac{2s}{L}\cdot\frac{L}{2\pi}\cdot\left(\frac{d\varepsilon}{dk}\right)^{-1} = \frac{1}{\pi}\,\frac{1}{ta\sin ka}$$

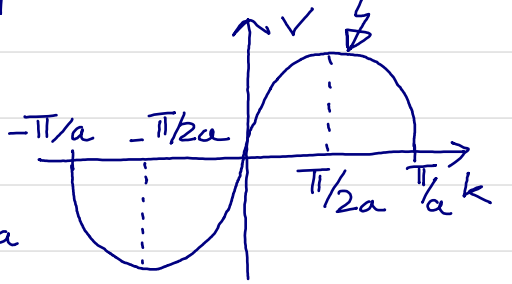
$$= \frac{1}{2\pi a}\cdot\frac{1}{\sqrt{4t^2-\varepsilon^2}}$$



→ van Hove singularities at $\pm 2t$

3° Semiclassical dynamics of Bloch wavepackets

Bragg scattering from lattice



$$|\psi(t)\rangle = \frac{1}{2\pi}\int dk\, w(k)\, e^{-i\varepsilon_k t/\hbar}\,|\psi_k\rangle$$

$$\psi(x,t) \equiv \langle x|\psi(t)\rangle$$

group velocity: $V = \frac{1}{\hbar}\frac{\partial \varepsilon_k}{\partial k} = \frac{2ta}{\hbar}\sin ka$

decoding notation: $V \Leftrightarrow \langle \hat{V}\rangle \equiv \int \psi^*(x)\,\frac{-i\hbar\partial/\partial x}{m}\,\psi(x)\,dx$

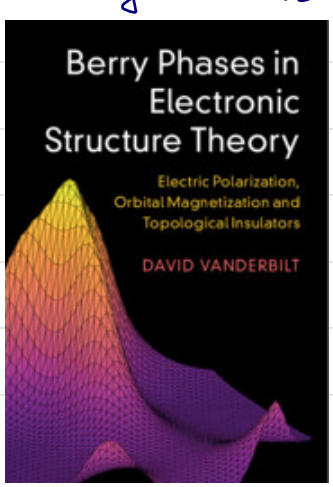
→ general expressions for any dimension including band index and Berry curvature effects

$$\psi(\vec{r}, t=0) = \int w(\vec{k}-\vec{k}_0)\, u^n_{\vec{k},\sigma}(\vec{r})\, d^3k$$

(band index; spin)

weight chosen to spread packet over many PUC

"semiclassical" means $\vec{k}_0$ and $\vec{r}_0$ are both well defined by neglecting uncertainty OR quantum interference over more than one classical path or within a closed orbit



↳ electron-lattice potential taken into account exactly by following crystal momentum

i) $\frac{d\langle\hat{\vec{k}}\rangle}{dt} = \frac{1}{\hbar}\vec{F}_{ext} = \frac{-e}{\hbar}\left(\vec{E} + \frac{d\langle\hat{\vec{r}}\rangle}{dt} \times \vec{B}\right)$ (electric field, magnetic field)

ii) $\frac{d\langle\hat{\vec{r}}\rangle}{dt} = \frac{1}{\hbar}\nabla_{\vec{k}}\,\varepsilon_\sigma^n(\vec{k})\Big|_{\vec{k}=\vec{k}_0} + \vec{\Omega}_\sigma^n(\vec{k}_0) \times \frac{d\langle\vec{k}\rangle}{dt}$ (anomalous velocity; $\vec{\Omega}_\sigma^n(\vec{k}_0)$: Berry curvature)

notation: $d\langle\hat{O}\rangle/dt = \frac{d}{dt}\langle\psi|\hat{O}|\psi\rangle$

iii) wavepackets stay in one band for sufficiently weak applied electric and magnetic fields

$\vec{F}_{ext} = 0 \Rightarrow \psi_{\vec{k}}$ can evolve only into $\psi_{\vec{k}+\vec{G}}$ or $c_1\psi^n_{\vec{k}} + c_2\psi^n_{\vec{k}+\vec{G}} + c_3\psi^m_{\vec{k}}$

↳ compare i) to free electron in plane wave $\psi(\vec{r}) \propto e^{i\vec{k}\cdot\vec{r}}$

$$d\langle\hat{\vec{p}}\rangle/dt = \vec{F}_{total} = \vec{F}_{ext} + \vec{F}_{lattice}$$

$$d\langle\hat{\vec{r}}\rangle/dt = \langle\hat{\vec{p}}\rangle/m$$

↳ in the case of Bloch wavepacket, electron-lattice interaction is capture by equation of motion for the expectation value of crystal momentum $\langle\hat{\vec{k}}\rangle$

△ BERRY CURVATURE: $\vec{\Omega}(\vec{k}) = \nabla \times \vec{A}(\vec{k})$ (Berry connection)

is geometrical property of Bloch eigenfunctions $\vec{A}(\vec{k}_0) = i\int_{PUC} d^3r \left[u^*_{\vec{k}}(\vec{r})\nabla_{\vec{k}} u_{\vec{k}}(\vec{r})\right]_{\vec{k}=\vec{k}_0}$

↳ $\vec{\Omega}^n_\sigma(\vec{k}) \neq 0$ iff { inversion symmetry is broken and/or; time-reversal symmetry is broken; spin-orbit coupling is strong }