

Tight-Binding Approach : fundamentals

A physicist point of view for theoretical chemists

Two different perspectives of the same problem

Starting from free electrons picture, we take into account for the periodicity of a weak potential
nearly-free electron model

Bloch theorem

band gap opening

Metal/semiconductor/insulator behavior

Starting from electrons in atomic orbitals (the potential is very strong), we take into account for the periodicity and the possible quantum tunneling process of an electron between two atoms seen as a perturbation.

Linear combination of atomic orbitals (LCAO)

Tight-binding approach

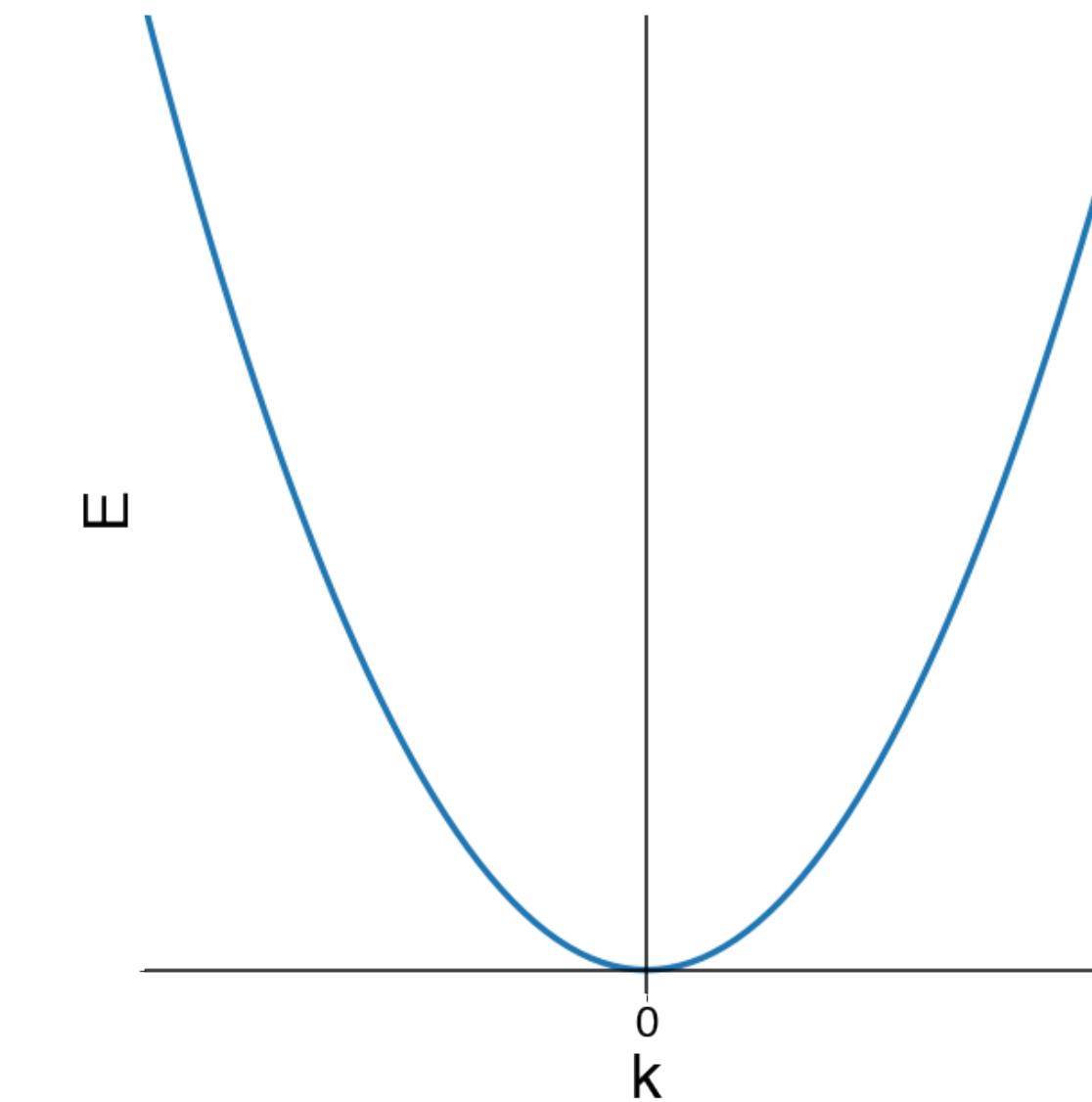
Nearly free electron model

Everything starts with a free electron

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad \text{with} \quad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$
$$\Psi(x) = A e^{ikx} \quad \text{or} \quad \Psi(x) = B e^{-ikx} \quad \text{for solutions}$$

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{dispersion curve}$$

k wave vector



Good model to describe metal properties

The problem of electrons in a solid is a many-electron problem
electron-atomic nuclei + electron-electron interactions

Electron in a periodic potential: Bloch's theorem

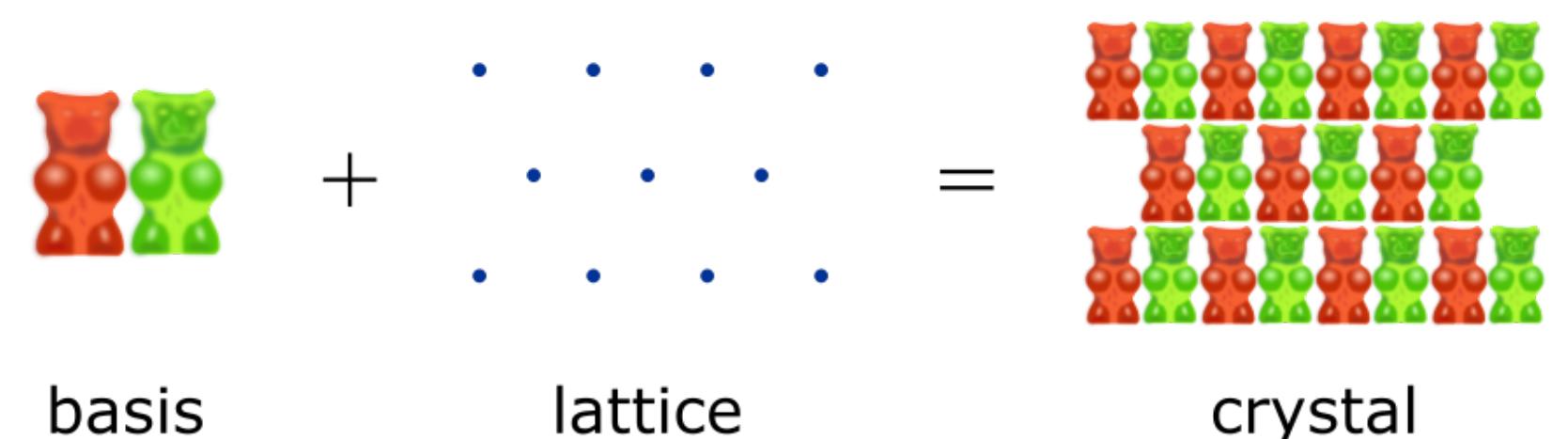
We now wish to introduce the effects of a periodic potential $\hat{V}(\vec{r})$. The underlying translational periodicity of the crystal is defined by the lattice translational vectors

$$\vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

where n_1, n_2, n_3 are integers

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ three non coplanar vectors (the primitive lattice translation vectors)

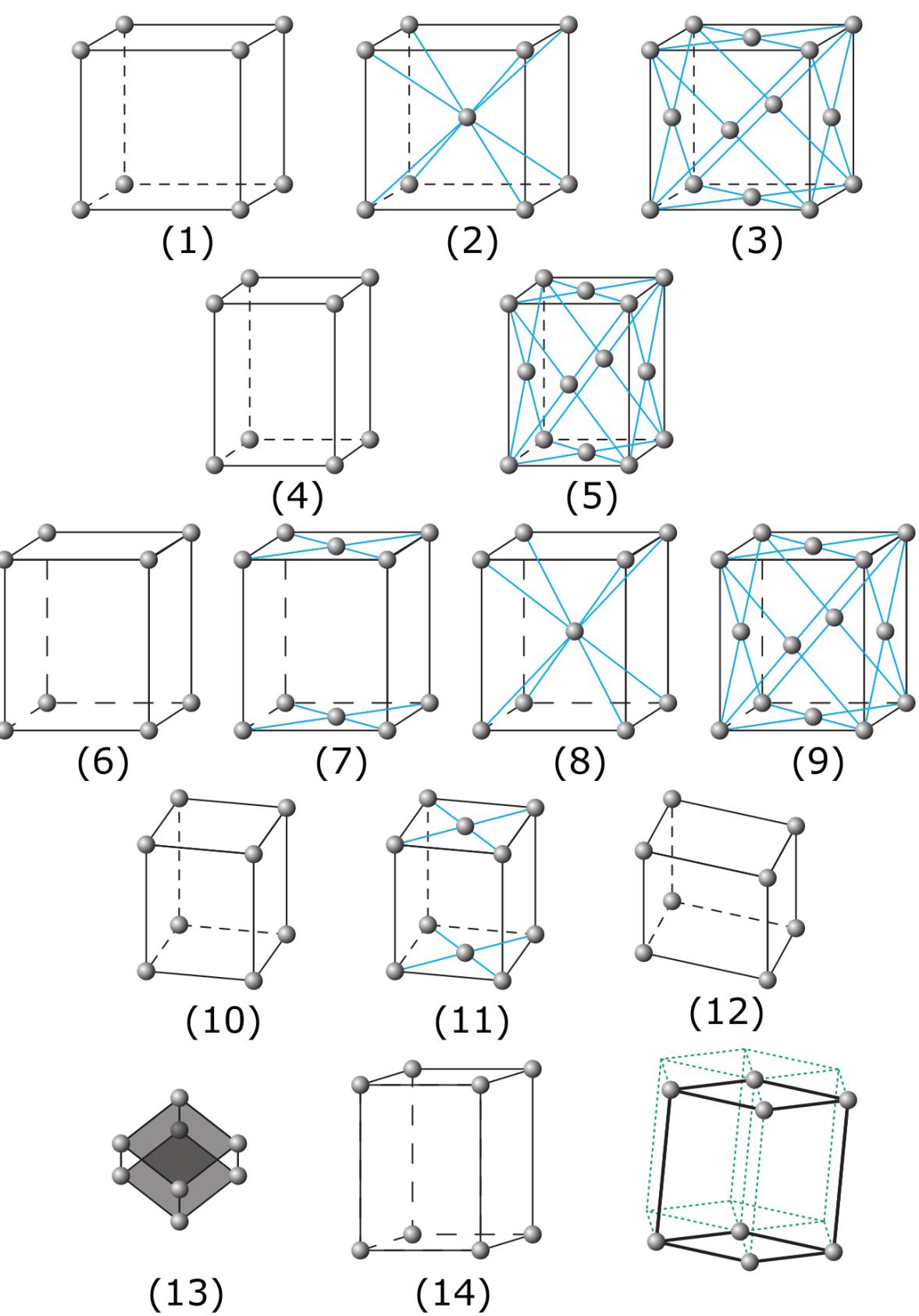
We recall: Structure of crystals = Bravais lattice + basis



Bravais lattice: set of translations that generates the entire periodic crystal

basis: positions and type of atoms in the primitive cell

$$\hat{V}(\vec{r}) = \hat{V}(\vec{r} + \vec{T})$$



Electron in a periodic potential: Bloch's theorem

The periodic nature of $\hat{V}(\vec{r})$ implies that the potential can be expressed as Fourier series

$$\hat{V}(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \quad \text{where } \vec{G} \text{ are a set of vectors and } V_{\vec{G}} \text{ are Fourier coefficients.}$$

$$\implies e^{i\vec{G}\cdot\vec{T}} = 1, \text{ i.e. } \vec{G}\cdot\vec{T} = 2\pi p \quad \text{where } p \text{ is an integer}$$

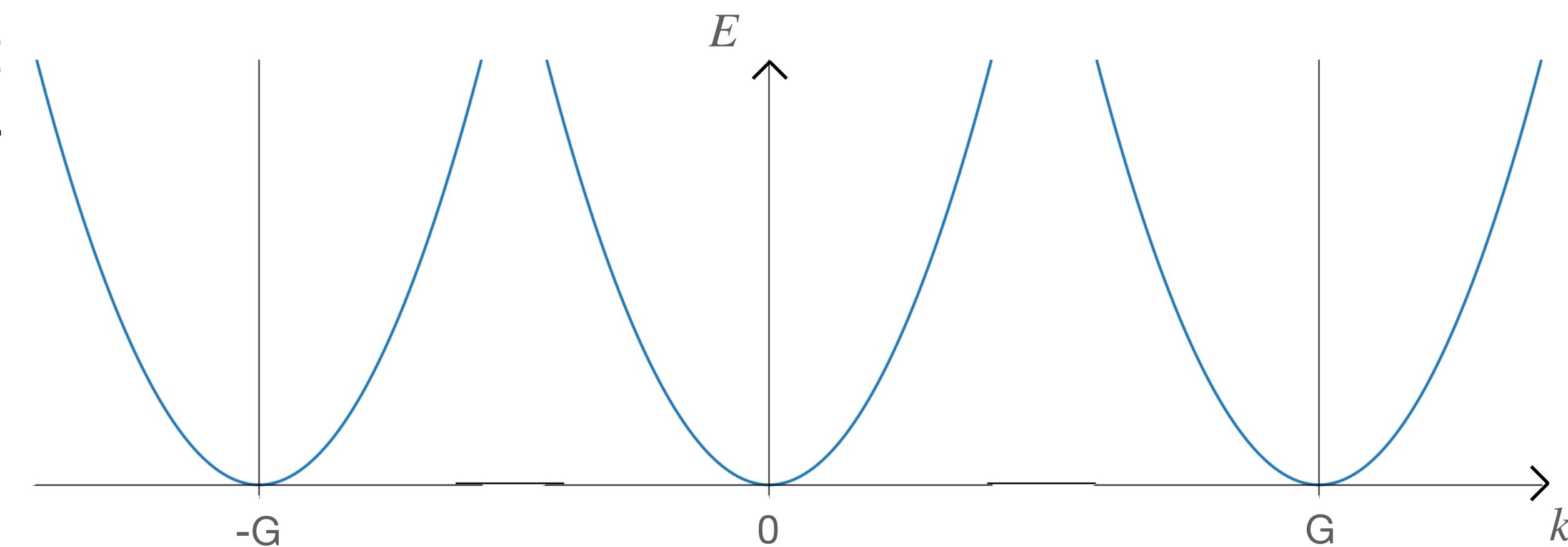
$$\implies \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$$

$$\implies \vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \quad \text{where } m_1, m_2, m_3 \text{ are integers}$$

The existence of a lattice in real space implies the existence of a lattice in reciprocal space defined by \vec{G} vectors. The \vec{b}_j are its primitive translation vectors.

Instead of dealing with one electron dispersion relationship $E(\vec{k})$, there must be an infinite number of equivalent dispersion relationships such that $E(\vec{k}) = E(\vec{k} + \vec{G})$, for all \vec{G} .

However the k -space periodicity also implies that all the information will be contained in the primitive unit of the reciprocal lattice, known as the first Brillouin zone (BZ).



Electron in a periodic potential: Bloch's theorem

The resulting Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}) \right] \Psi(\vec{r}) = E\Psi(\vec{r})$$

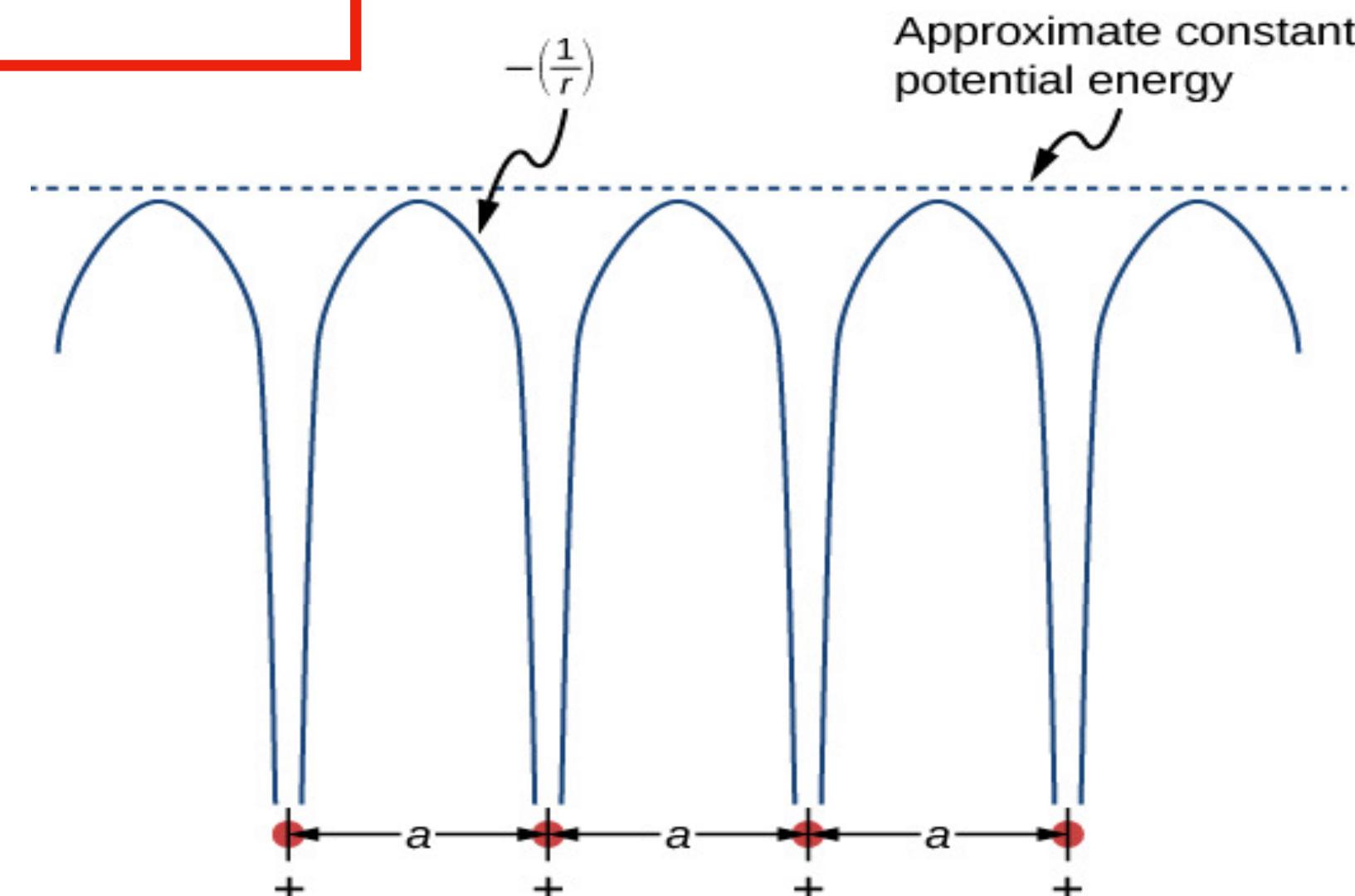
Born-von Karman periodic boundary conditions (PBC)

We choose a plane wave $\phi(\vec{r}) = e^{i(\vec{k} \cdot \vec{r} - \omega t)}$ subject to PBC $\phi(\vec{r} + N_j \vec{a}_j) = e^{i(\vec{k} \cdot \vec{r} - \omega t)} \Rightarrow e^{iN_j \vec{k} \cdot \vec{a}_j} = 1 \Rightarrow \vec{k} = \sum_{j=1}^3 \frac{m_j}{N_j} \vec{b}_j$
where N_j is the number of units cells in the j^{th} direction

We can built wavefunctions that satisfies the PBC:

$$\Psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

Allowed wavevectors



Example of 1D potential (linear chain of atoms)

Electron in a periodic potential: Bloch's theorem

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}) \right] \Psi(\vec{r}) = E \Psi(\vec{r})$$

$$\sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \left\{ \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \right\} \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} = E \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

$$\sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \sum_{\vec{k}} \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}} e^{i(\vec{G}+\vec{k})\cdot\vec{r}} = E \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

$$\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \left\{ \left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} \right\} = 0$$

Central equation

$$\boxed{\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0}$$

If one set the potential to zero (vanishing potential) the equation turns out to be the one of the free electron model
Assuming that Fourier coefficients $V_{\vec{G}}$ decay in magnitude as grows $||\vec{G}||$, one ends with a finite number of $C_{\vec{k}-\vec{G}}$
Just to deal with solutions in the first BZ, we can write $\vec{k} = \vec{q} - \vec{G}'$ and $\vec{G}'' = \vec{G} + \vec{G}'$

$$\left(\frac{\hbar^2 \left| \left| \vec{q} - \vec{G}' \right| \right|^2}{2m} - E \right) C_{\vec{q}-\vec{G}'} + \sum_{\vec{G}''} V_{\vec{G}''-\vec{G}'} C_{\vec{q}-\vec{G}''} = 0$$

Electron in a periodic potential: Bloch's theorem

If we choose a particular value of \vec{q} , then the only $C_{\vec{k}}$ that feature the previous equation are of the form $C_{\vec{q}-\vec{G}}$

Therefore for each distinct value of \vec{q} , there is a wavefunction $\Psi_{\vec{q}}(\vec{r})$ that takes the form

$$\Psi_{\vec{q}}(\vec{r}) = e^{i\vec{q} \cdot \vec{r}} \sum_{\vec{G}} C_{\vec{q}-\vec{G}} e^{-i\vec{G} \cdot \vec{r}} = e^{i\vec{q} \cdot \vec{r}} u_{j,\vec{q}}$$

The wavefunction can be rewritten in terms of a product of a plane wave with the wavevector within the first BZ and a periodical function associated to the lattice.

This is the Bloch theorem

An important consequence of the Bloch theorem is the appearance of the energy bands, due to the eigenvalue problem arising when replacing the Bloch function in the Schrödinger equation

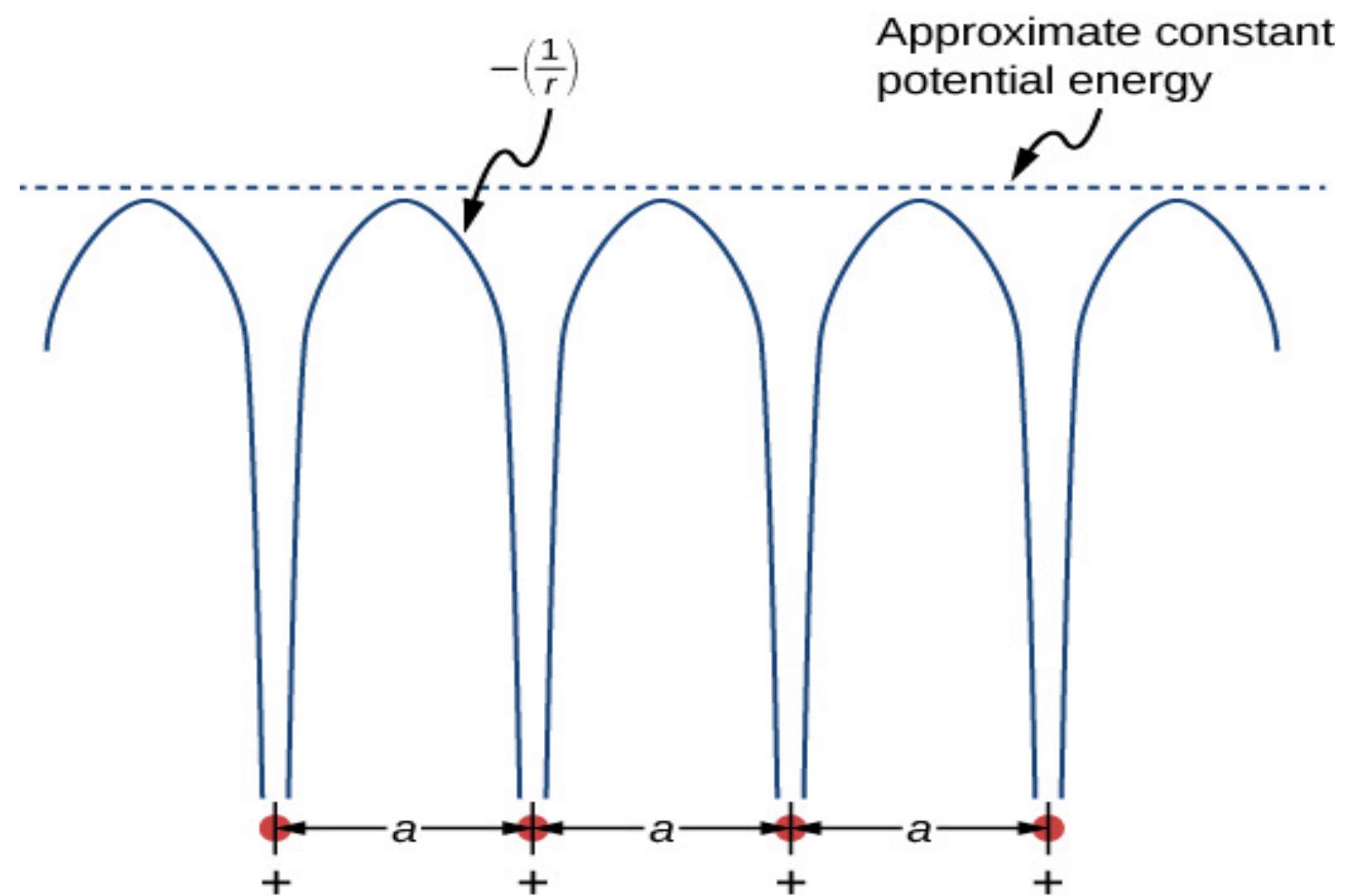
$$\hat{H}(\vec{k}) u_{\vec{k}}(\vec{r}) = \left[-\frac{\hbar^2}{2m} (i\vec{k} + \nabla)^2 + \hat{V}(\vec{r}) \right] u_{\vec{k}}(\vec{r}) = E(\vec{k}) u_{\vec{k}}(\vec{r})$$

Because the eigenvalue problem is set in a fixed finite volume, we expect on general grounds to find an infinite family of solutions with discretely spaced eigenvalues, which we label with the band index n .

The Bloch function can therefore be denoted by $\Psi_{n,\vec{k}}(\vec{r})$ which indicates that each value of the band index n and the vector \vec{k} specifies an electron state, or an orbital with energy $E_n(\vec{k})$.

Nearly-free electron model 1D

In the nearly-free electrons model, we consider an independent electron approximation, assuming that all the interactions are described by an effective potential that is periodic $\hat{V}(\vec{r}) = \hat{V}(\vec{r} + \vec{T})$ but remains weak.



It is time to solve the problem !

$$\left(\frac{\hbar^2 \left| \vec{q} - \vec{G}' \right|^2}{2m} - E \right) C_{\vec{q}-\vec{G}'} + \sum_{\vec{G}''} V_{\vec{G}''-\vec{G}'} C_{\vec{q}-\vec{G}''} = 0$$

Free electron energy of a state with $\vec{k} = \vec{q} - \vec{G}$ as

$$E_{\vec{q}-\vec{G}'}^0 = \frac{\hbar^2 \left| \vec{q} - \vec{G}' \right|^2}{2m}$$

$$\left(E_{\vec{q}-\vec{G}'}^0 - E \right) C_{\vec{q}-\vec{G}'} + \sum_{\vec{G}'' \neq \vec{G}'} V_{\vec{G}''-\vec{G}'} C_{\vec{q}-\vec{G}''} = 0$$

Nearly-free electron model 1D

A single electron energy state defined by $E(\vec{q} - \vec{G}')$: no other states at the same energy at that point in k-space

Vanishing potential: $V_{\vec{G}} \rightarrow 0$

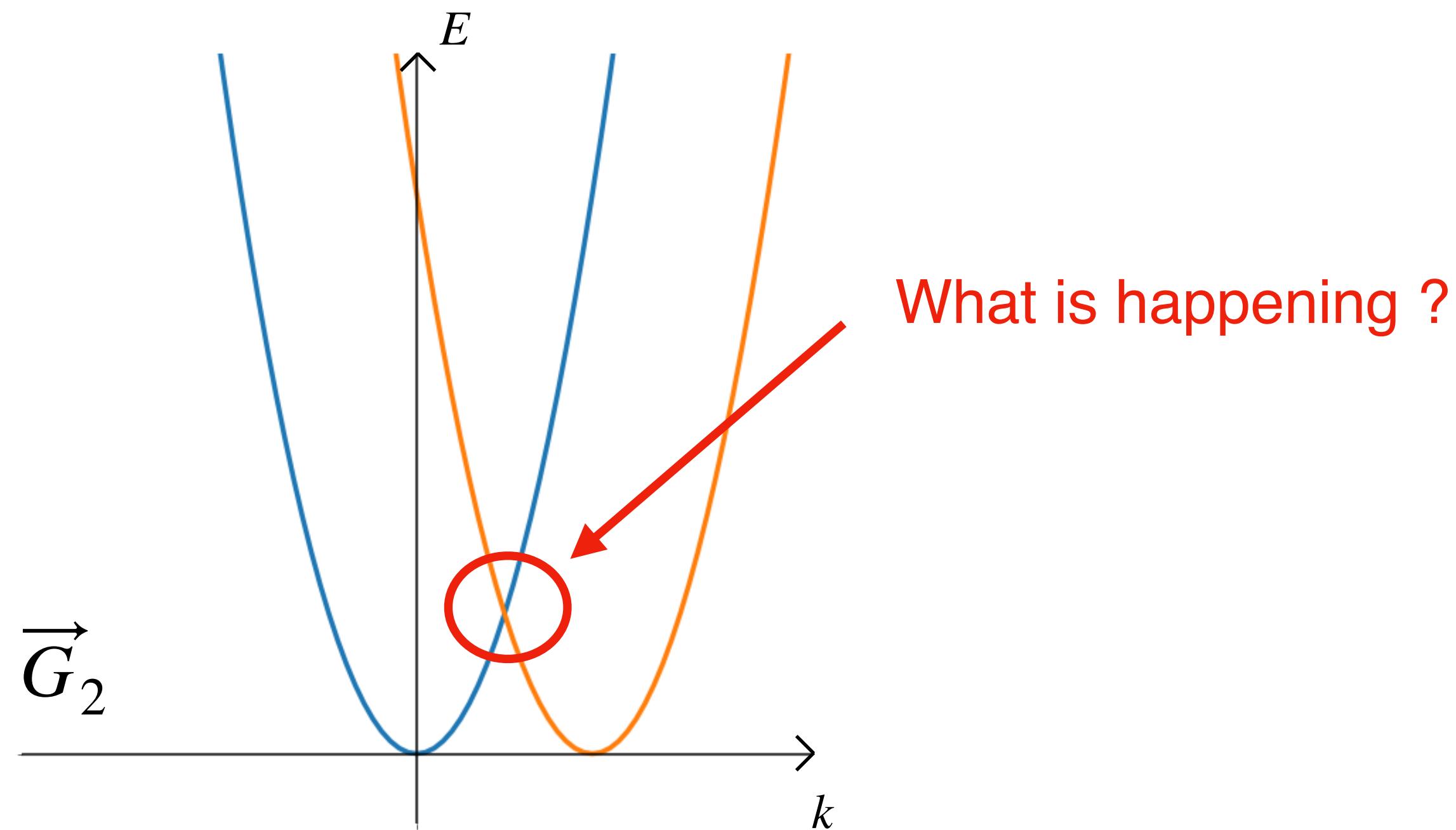
$$\left(E_{\vec{q}-\vec{G}'}^0 - E \right) C_{\vec{q}-\vec{G}'} = 0 \implies E(\vec{q} - \vec{G}') = E_{\vec{q}-\vec{G}'}^0 = \frac{\hbar^2 \|\vec{q} - \vec{G}'\|^2}{2m}$$

Spatial part of the wavefunction being a single plane wave

Two degenerate free-electron levels

$$\left| E_{\vec{q}-\vec{G}_1}^0 - E_{\vec{q}-\vec{G}_2}^0 \right| \leq V$$

$$\left| E_{\vec{q}-\vec{G}_1}^0 - E_{\vec{q}-\vec{G}}^0 \right| \gg V \text{ For all other } \vec{G} \neq \vec{G}_2$$



Nearly-free electron model 1D

$$\begin{cases} \left(E - E_{\vec{q}-\vec{G}_1}^0\right) C_{\vec{q}-\vec{G}_1} = V_{\vec{G}_2-\vec{G}_1} C_{\vec{q}-\vec{G}_2} + \sum_{\vec{G} \neq \vec{G}_1, \vec{G}_2} V_{\vec{G}-\vec{G}_1} C_{\vec{q}-\vec{G}} \\ \left(E - E_{\vec{q}-\vec{G}_2}^0\right) C_{\vec{q}-\vec{G}_2} = V_{\vec{G}_1-\vec{G}_2} C_{\vec{q}-\vec{G}_1} + \sum_{\vec{G} \neq \vec{G}_1, \vec{G}_2} V_{\vec{G}-\vec{G}_2} C_{\vec{q}-\vec{G}} \end{cases}$$

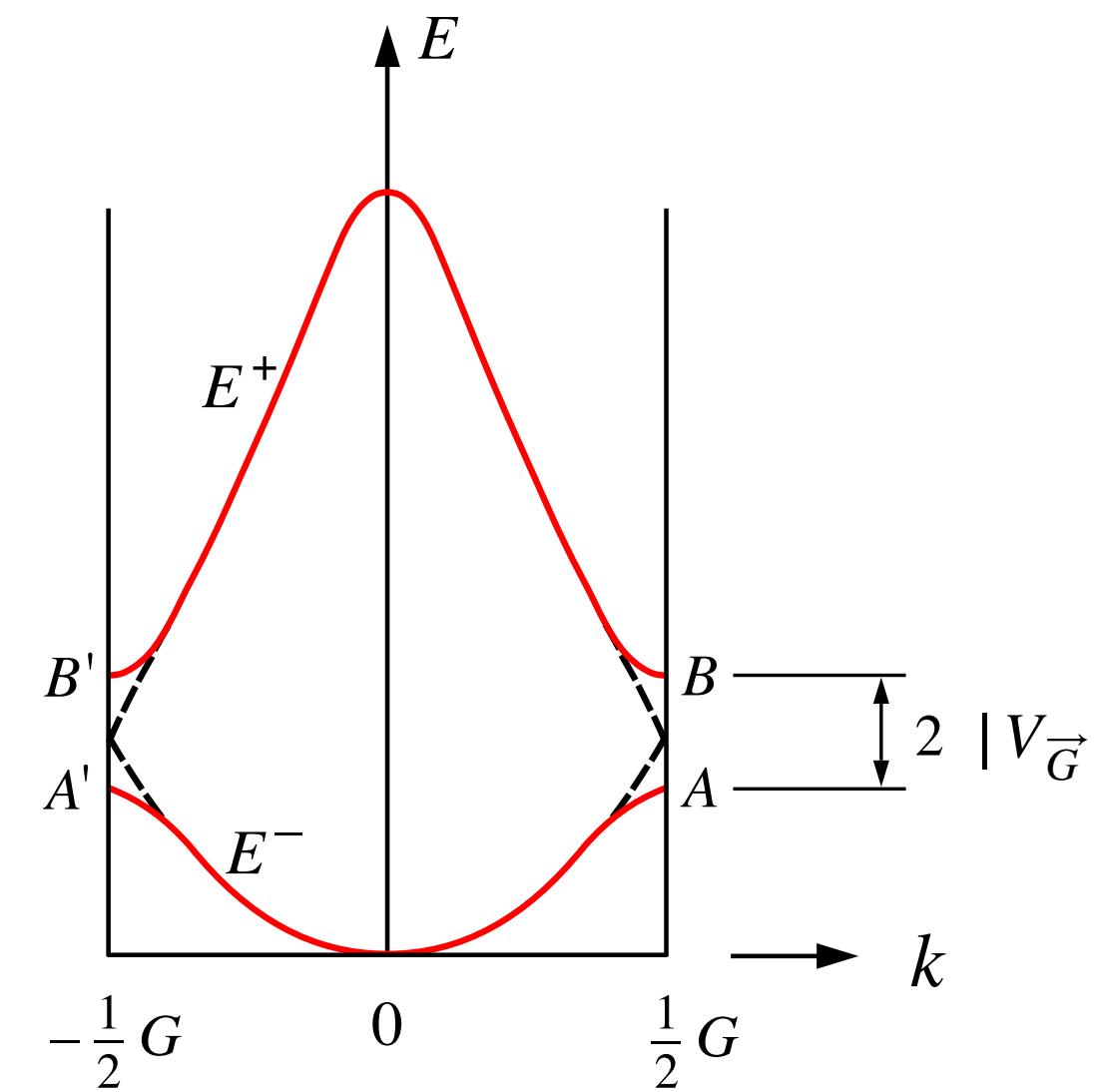
$$\begin{cases} \left(E - E_{\vec{q}-\vec{G}_1}^0\right) C_{\vec{q}-\vec{G}_1} = V_{\vec{G}_2-\vec{G}_1} C_{\vec{q}-\vec{G}_2} \\ \left(E - E_{\vec{q}-\vec{G}_2}^0\right) C_{\vec{q}-\vec{G}_2} = V_{\vec{G}_1-\vec{G}_2} C_{\vec{q}-\vec{G}_1} \end{cases}$$

Simplification of the notation : $\vec{k} = \vec{q} - \vec{G}_1$, $\vec{G} = \vec{G}_2 - \vec{G}_1$

$$\begin{cases} \left(E - E_{\vec{k}}^0\right) C_{\vec{k}} = V_{\vec{G}} C_{\vec{k}-\vec{G}} \\ \left(E - E_{\vec{k}-\vec{G}}^0\right) C_{\vec{k}-\vec{G}} = V_{\vec{G}}^* C_{\vec{k}} \end{cases}$$

$$\begin{vmatrix} \left(E - E_{\vec{k}}^0\right) & V_{\vec{G}} \\ V_{\vec{G}}^* & \left(E - E_{\vec{k}-\vec{G}}^0\right) \end{vmatrix} = 0$$

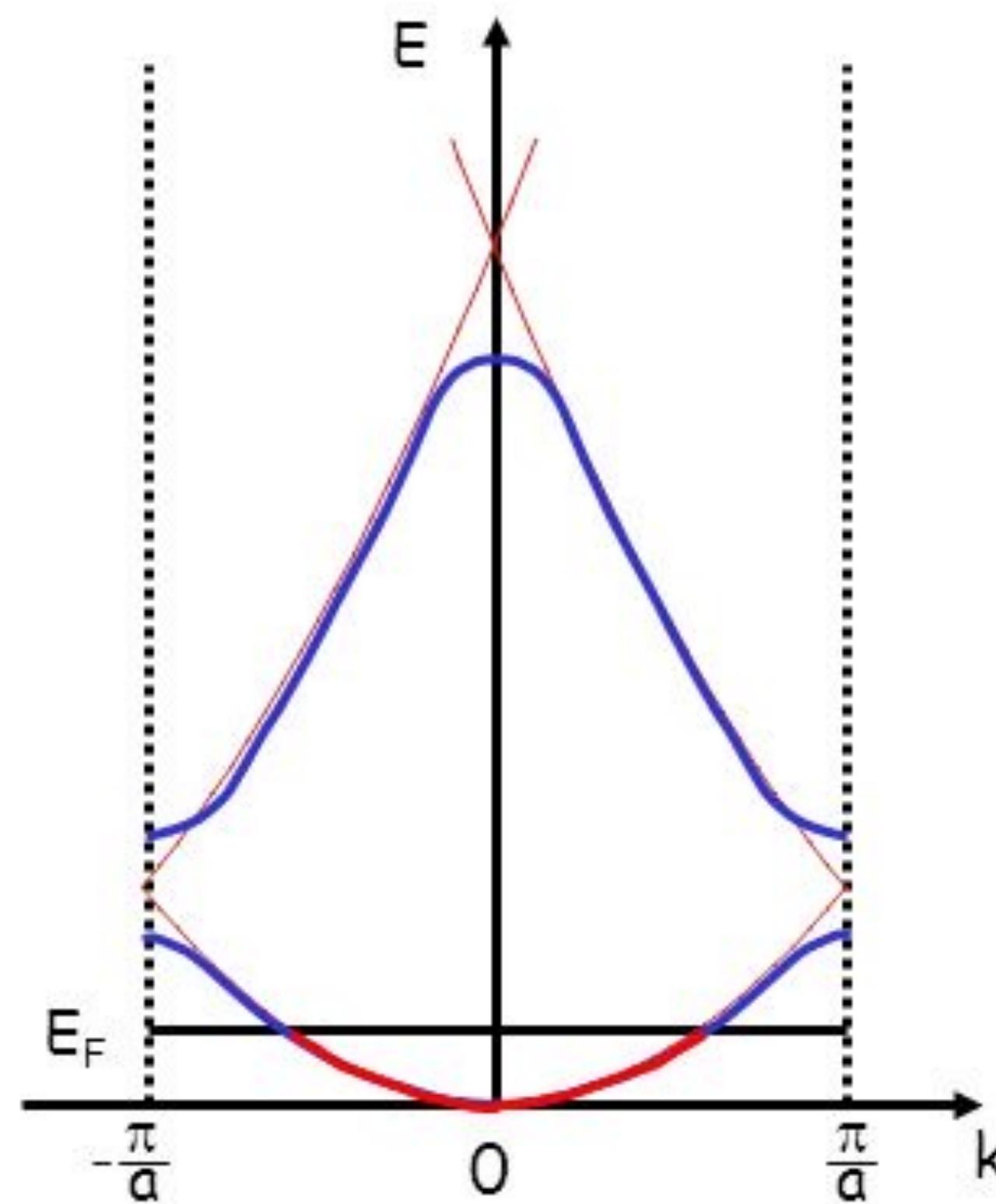
$$E = \frac{1}{2} \left(E_{\vec{k}}^0 + E_{\vec{k}-\vec{G}}^0 \right) \pm \left[\left(\frac{E_{\vec{k}}^0 - E_{\vec{k}-\vec{G}}^0}{2} \right)^2 + |V_{\vec{G}}|^2 \right]^{\frac{1}{2}}$$



Gap opening

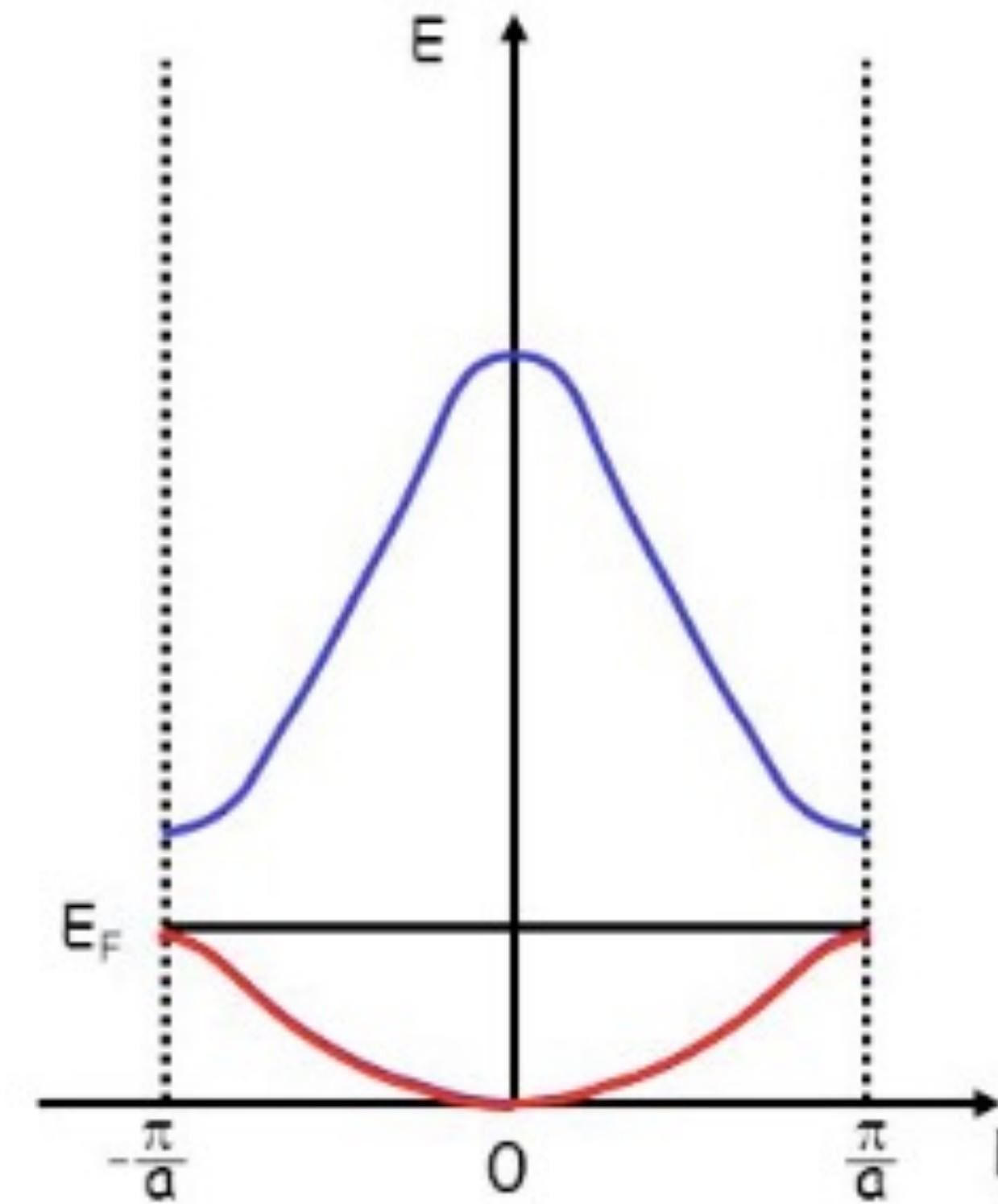
Metal, semi-conductors and insulators

Metal



Atoms with one valence electron

Semi-conductor/insulator



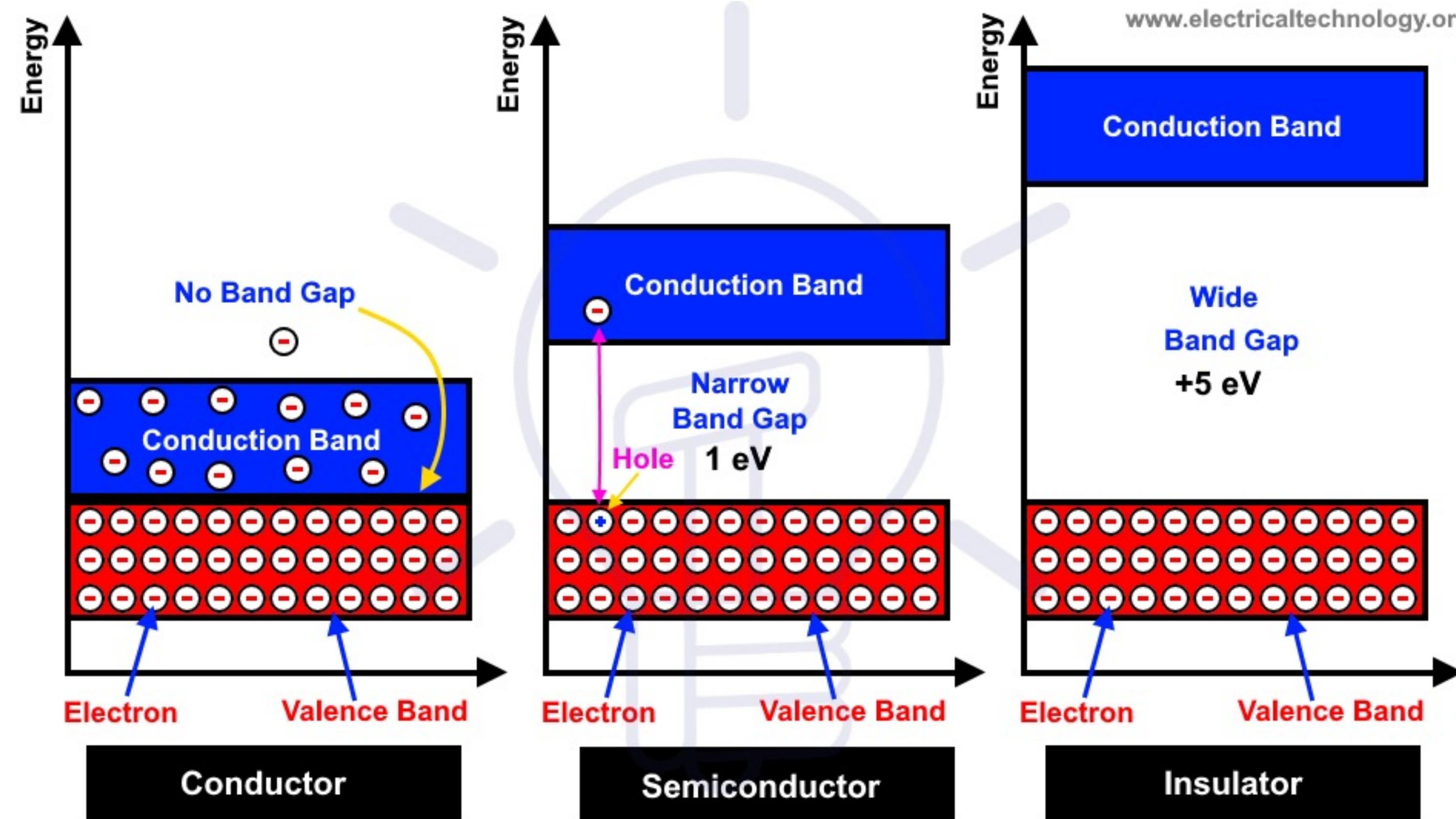
Atoms with two valence electrons

The number of electronic states in a band is equal to the number of unit cells N in the crystal.

Since each state can accommodate at most two electrons, of opposite spins, it follows that the maximum number of electrons that may occupy a single band is $2N$.

Metal, semi-conductors and insulators

Generalization



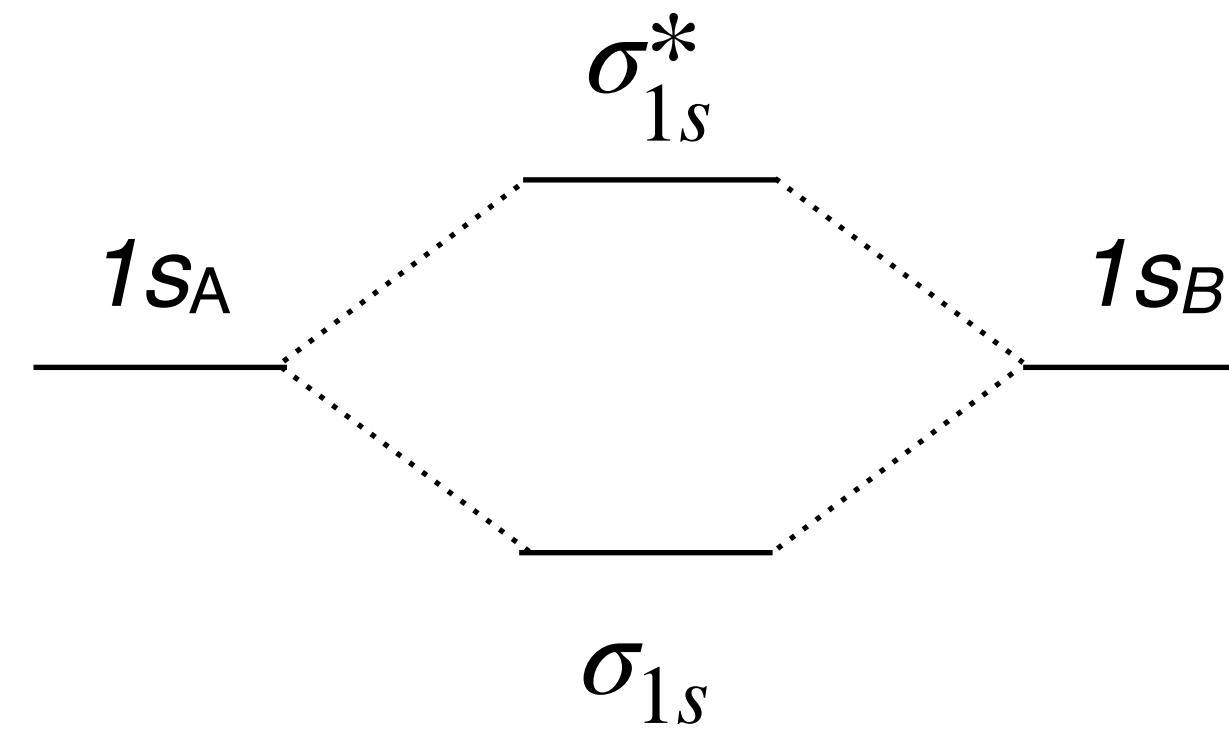
Tight binding approach

From atoms to solids

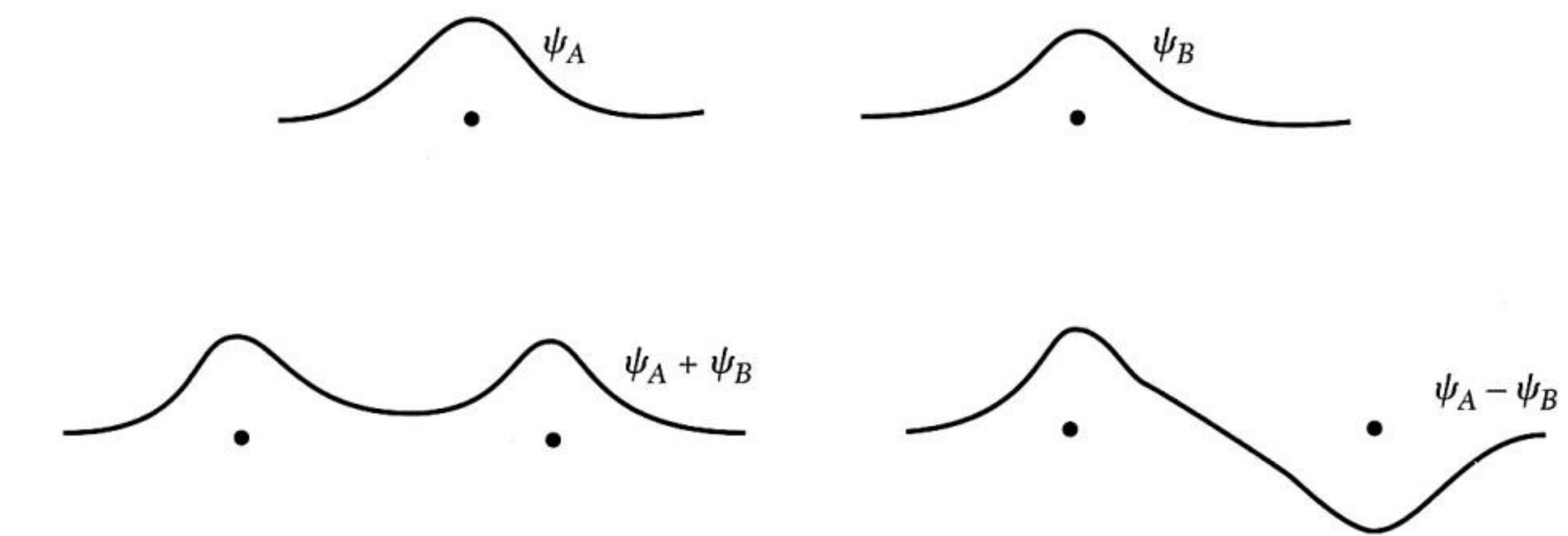
Let's start with neutral separated atoms and watch the changes in the atomic energy levels as the charge distributions of adjacent atoms overlap when atoms are brought together to form a crystal

Consider two H atoms, each with an electron in the $1s$ state

Energy diagram



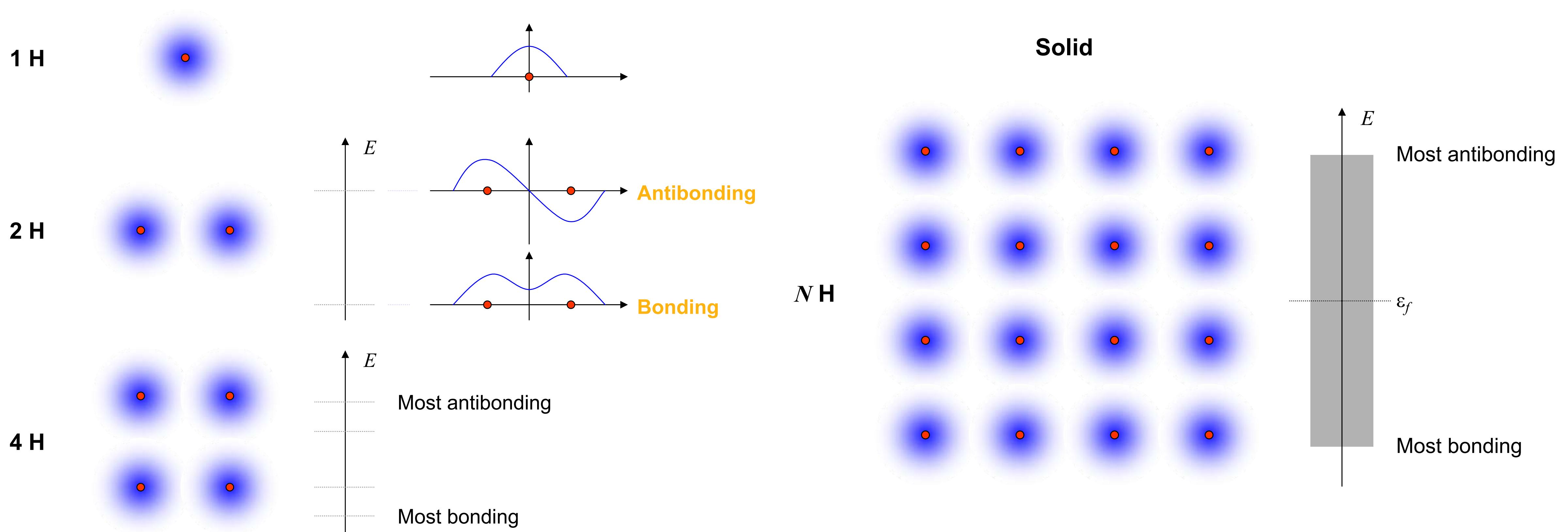
Wavefunction combination



The atomic Hamiltonian \hat{H}_{at} will be the first elementary brick

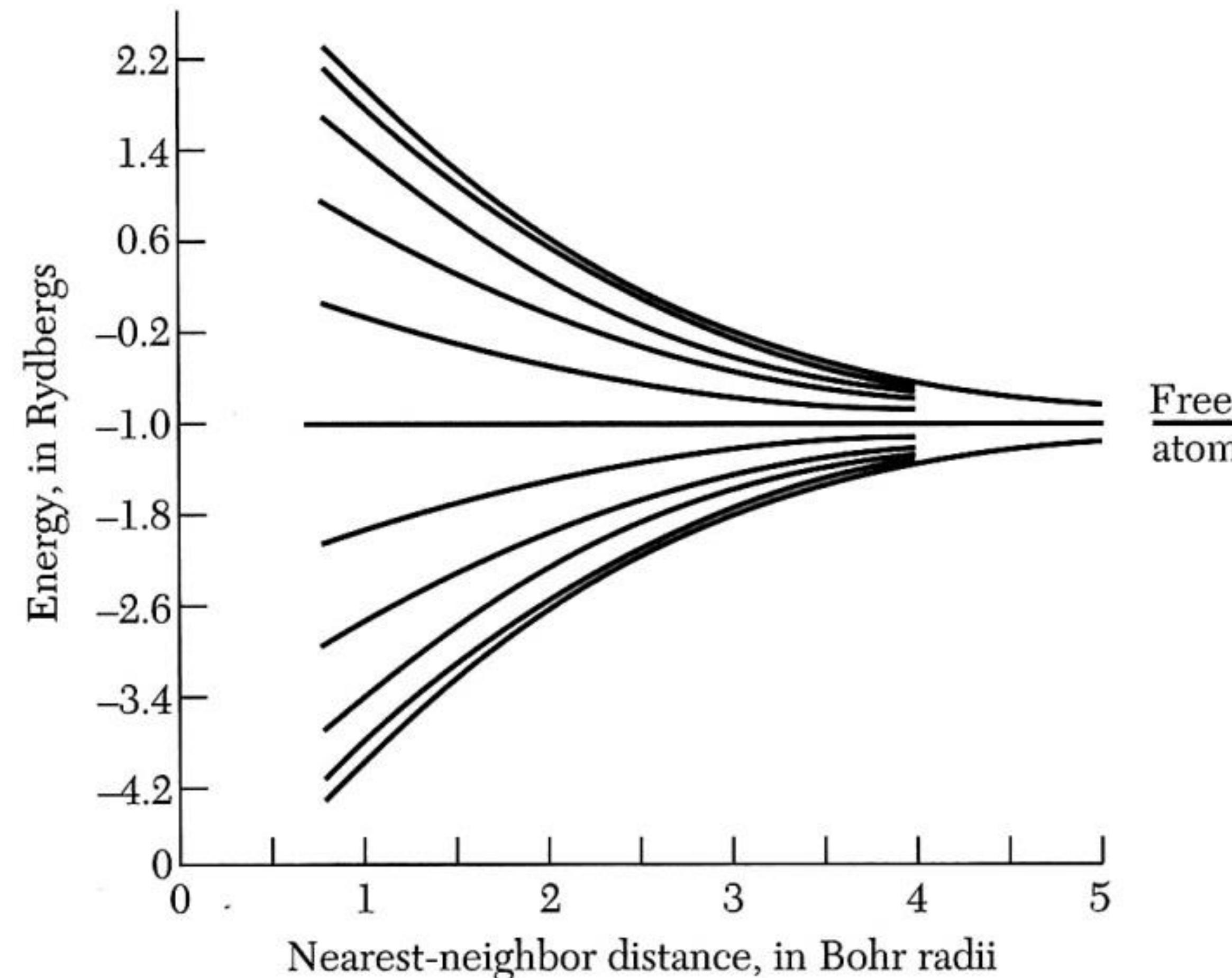
$$\hat{H}_{at} |\phi_j(\vec{r})\rangle = \epsilon_j |\phi_j(\vec{r})\rangle$$

From atoms to solids



Energy band broadening

The broadening of the $1s$ band for a ring of 20 H atoms with respect to the interatomic distance



Basic definitions

The potentials involved are : — the actual crystal potential $\hat{V}(\vec{r})$

— the potential associated with an isolated atom $\hat{V}_0(\vec{r})$

To first order, the crystal Hamiltonian is $\hat{H} = \hat{H}_{at} + (\hat{V}(\vec{r}) - \hat{V}_0(\vec{r})) = \hat{H}_{at} + \Delta\hat{V}(\vec{r})$

with $\hat{H}\Psi_{\vec{k}}(\vec{r}) = E(\vec{k})\Psi_{\vec{k}}(\vec{r})$

Let μ label the atoms in the primitive cell and α label the orbitals on a given atom.

Let the TB basis orbitals be $\varphi_{\mu\alpha}(\vec{r} - \vec{T} - \vec{t}_\mu)$ where \vec{t}_μ is the location of atom μ in the home unit cell.

$$\vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \text{ is a lattice vector}$$

We now introduce a compound index $j = \{\mu\alpha\}$ that runs over all the L TB orbitals in the primitive cell, and define:

$$\phi_{\vec{T}j}(\vec{r}) = \phi_j(\vec{r} - \vec{T}) = \varphi_{\mu\alpha}(\vec{r} - \vec{T} - \vec{t}_\mu)$$

to be the TB basis orbital of type j in cell \vec{T} . From now on we drop indices $\mu\alpha$ and work only with j , letting $\vec{t}_\mu \rightarrow \vec{t}_j$.

Minimal (orthogonal) TB model

The basis orbitals are orthonormal: $\langle \phi_{\vec{T}i} | \phi_{\vec{T}'j} \rangle = \delta_{\vec{T}\vec{T}'} \delta_{ij}$

The position matrix have the simplest possible form: $\langle \phi_{\vec{T}i} | \vec{r} | \phi_{\vec{T}'j} \rangle = (\vec{T} + \vec{t}_j) \delta_{\vec{T}\vec{T}'} \delta_{ij}$

The Hamiltonian is assumed to have translational symmetry, so that its matrix elements are defined via:

$$H_{ij}(\vec{T}) = \langle \phi_{\vec{T}i} | \hat{H} | \phi_{\vec{T}'j} \rangle = \langle \phi_{\vec{0}i} | \hat{H} | \phi_{\vec{T}j} \rangle$$

and we assume that $H_{ij}(\vec{T})$ decays rapidly with increasing \vec{T} .

Transition to the Bloch representation

We construct Bloch-like basis functions $\chi_{j,\vec{k}}(\vec{r}) = \sum_{\vec{T}} e^{i\vec{k} \cdot (\vec{T} + \vec{t}_j)} \phi_j(\vec{r} - \vec{T})$

In the bra-ket language : $|\chi_{j,\vec{k}}\rangle = \sum_{\vec{T}} e^{i\vec{k} \cdot (\vec{T} + \vec{t}_j)} |\phi_{\vec{T}j}\rangle$

Normalization is to a single unit cell: $\langle \chi | \chi' \rangle = \int_{\text{cell}} d^3 r \chi^*(\vec{r}) \chi(\vec{r}') \implies \langle \chi_{i,\vec{k}} | \chi_{j,\vec{k}} \rangle = \delta_{ij}$

The Bloch eigenstates are then expanded as $|\Psi_{n,\vec{k}}\rangle = \sum_j C_{j,n,\vec{k}} |\chi_{j,\vec{k}}\rangle$

and the Hamiltonian matrix is constructed as $H_{ij,\vec{k}} = \langle \chi_{i,\vec{k}} | \hat{H} | \chi_{j,\vec{k}} \rangle = \sum_{\vec{T}} e^{i\vec{k} \cdot (\vec{T} + \vec{t}_j - \vec{t}_i)} H_{ij}(\vec{T})$

H_{ii} is an on-site energy

H_{ij} is hopping term

Transition to the Bloch representation

The secular equation to be solved is

$$H_{\vec{k}} C_{n,\vec{k}} = E_{n,\vec{k}} C_{n,\vec{k}}$$

where $H_{\vec{k}}$ is the $L \times L$ matrix of elements $H_{ij,\vec{k}}$ and $C_{n,\vec{k}}$ is the column vector of elements $C_{j,n,\vec{k}}$

This secular equation can be straightforwardly diagonalized to give the TB solution for the energy eigenvalues and eigenvectors. Of course, this TB solution only produces L bands, where L is the number of TB basis orbitals per cell, representing an approximation to the L bands of the crystal that are built from these TB orbitals (usually these are the L lowest valence and conduction bands).

Hamiltonian construction

$$E_{n,\vec{k}} = \sum_{\vec{T}} e^{-i\vec{k}\cdot\vec{T}} \int d^3r \Psi_{n,\vec{k}}^*(\vec{r}) H_{\vec{k}}(\vec{r}) \Psi_{n,\vec{k}}(\vec{r})$$

$$E_{n,\vec{k}} = \sum_{\vec{T}} e^{-i\vec{k}\cdot\vec{T}} \int d^3r \phi_n^*(\vec{r} - \vec{T}) H_{\vec{k}}(\vec{r}) \Psi_{n,\vec{k}}(\vec{r}) \quad \phi_n^*(\vec{r} - \vec{T}) = \phi_{\vec{T}n}^*$$

$$E_{n,\vec{k}} = \sum_{\vec{T}'} \sum_{\vec{T}} e^{-i\vec{k}\cdot\vec{T}} \int d^3r \phi_n^*(\vec{r} - \vec{T}) H_{at}(\vec{r} - \vec{T}') \Psi_{n,\vec{k}}(\vec{r}) + \sum_{\vec{T}} e^{-i\vec{k}\cdot\vec{T}} \int d^3r \phi_n^*(\vec{r} - \vec{T}) \Delta V(\vec{r}) \Psi_{n,\vec{k}}(\vec{r})$$

$$E_{n,\vec{k}} = \epsilon_n - \beta_n + \sum_{\vec{T} \neq \vec{0}} \sum_l e^{i\vec{k}\cdot\vec{T}} \gamma_{n,l}(\vec{T})$$

$\beta_n = - \int d^3r \phi_n^*(\vec{r}) \Delta V(\vec{r}) \phi_n(\vec{r})$ is the atomic energy shift due to the potential on neighboring atoms.

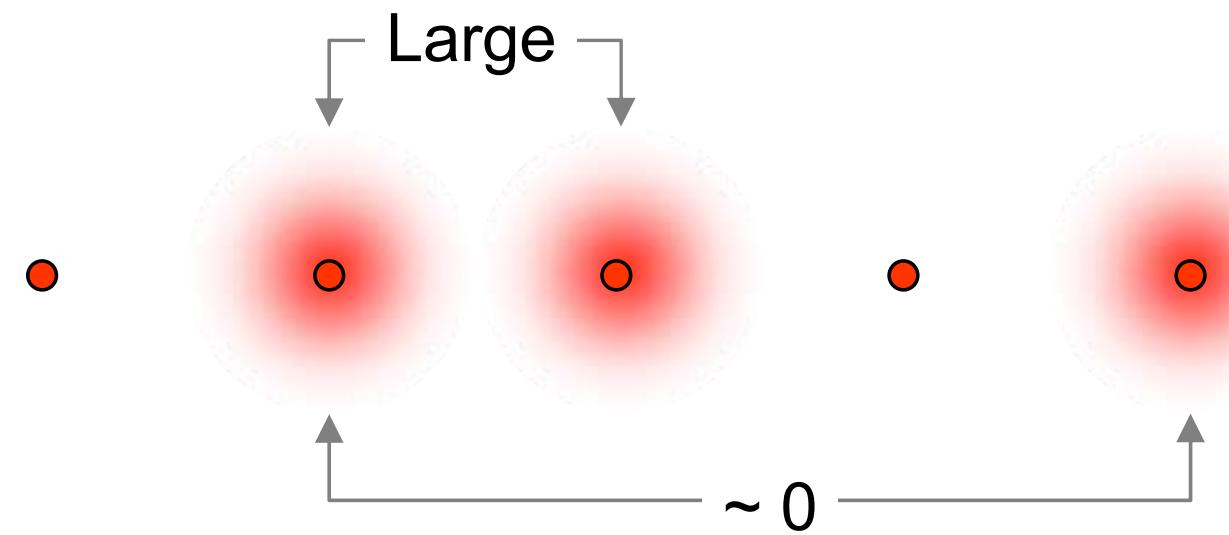
$\gamma_{n,l}(\vec{T}) = - \int d^3r \phi_n^*(\vec{r}) \Delta V(\vec{r}) \phi_l(\vec{r} - \vec{T})$ is the interatomic matrix element between the atomic orbitals m and l on adjacent atoms.

It is also called the bond energy or two center integral usually taken from Slater and Koster work (1954)

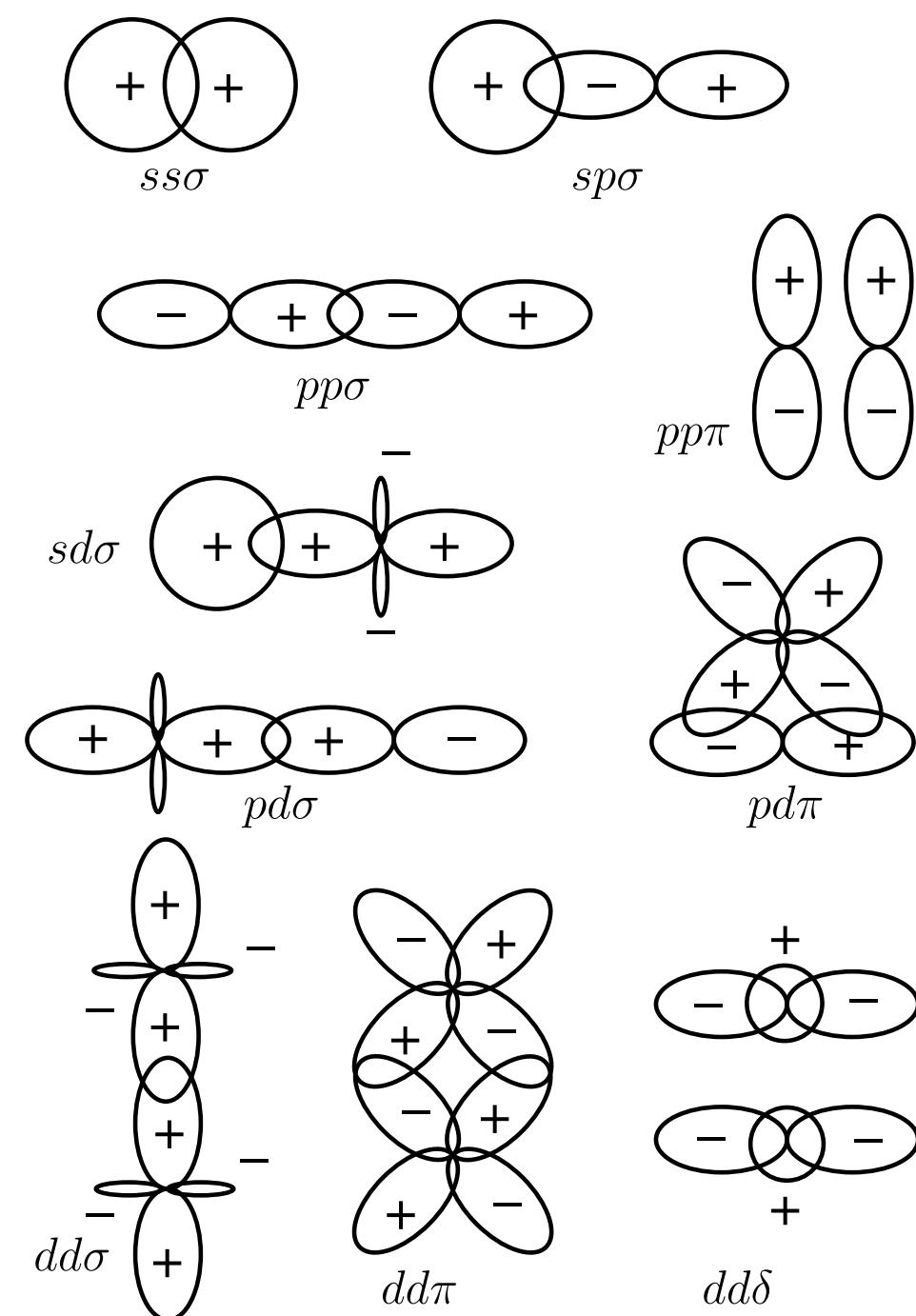
Standard approach

The Hamiltonian matrix elements decrease very fast with increasing $\| \vec{T} \|$

Assume zero Hamiltonian matrix elements beyond first, second or third nearest neighbors.

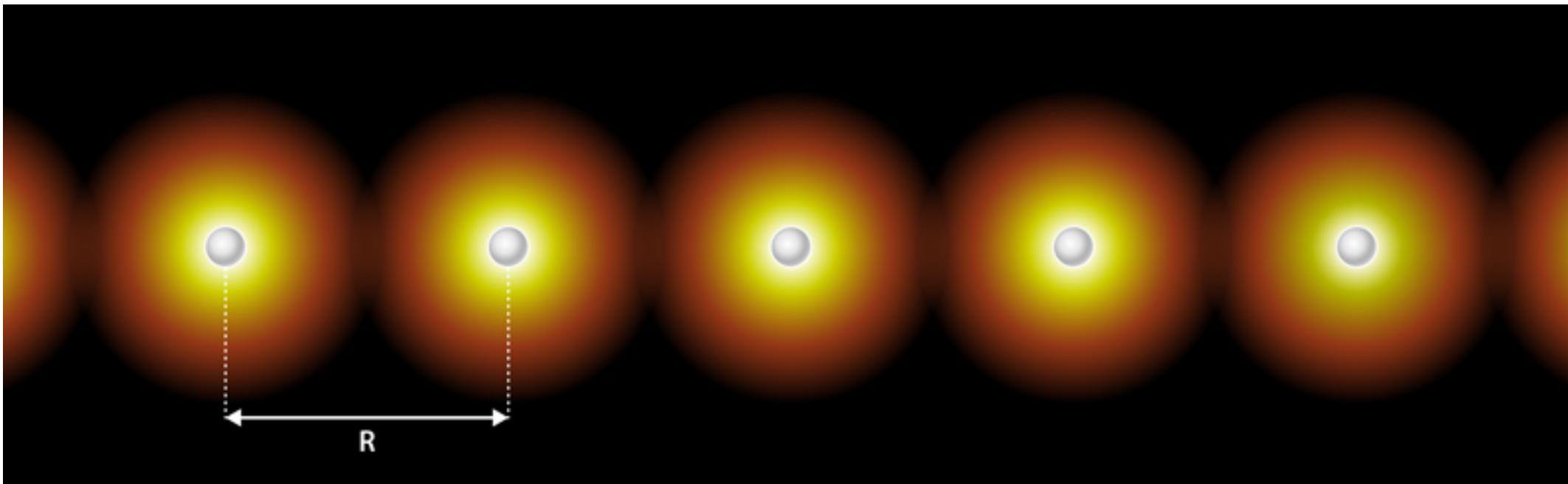


Bond integrals



One 1D s-band

A string of atoms with a single s -orbital in a straight line with spacing R and σ bonds between atomic sites:
a linear chain of H atoms



N total number of sites
 k is a real parameter

$$-\frac{\pi}{R} \leq k \leq \frac{\pi}{R}$$

Let's build the LCAO to find the eigenstates of the Hamiltonian $|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{inkR} |n\rangle$

Assuming only nearest neighbor hopping: the only non-zero matrix elements are:

$\langle n | \hat{H} | n \rangle = E_0 = E_i - U$ The energy E_i is the ionization energy corresponding to the chosen atomic orbital
 U is the energy shift of the orbital as a result of the potential of neighboring atoms

$\langle n \pm 1 | \hat{H} | n \rangle = -\Delta$ are the Slater and Koster interatomic matrix elements, *i.e.* the bond energies $E_{i,j}$. In this one dimensional s-band model we only have σ -bonds between the s -orbitals with bond energy $E_{s,s} = V_{ss\sigma}$

One 1D s-band

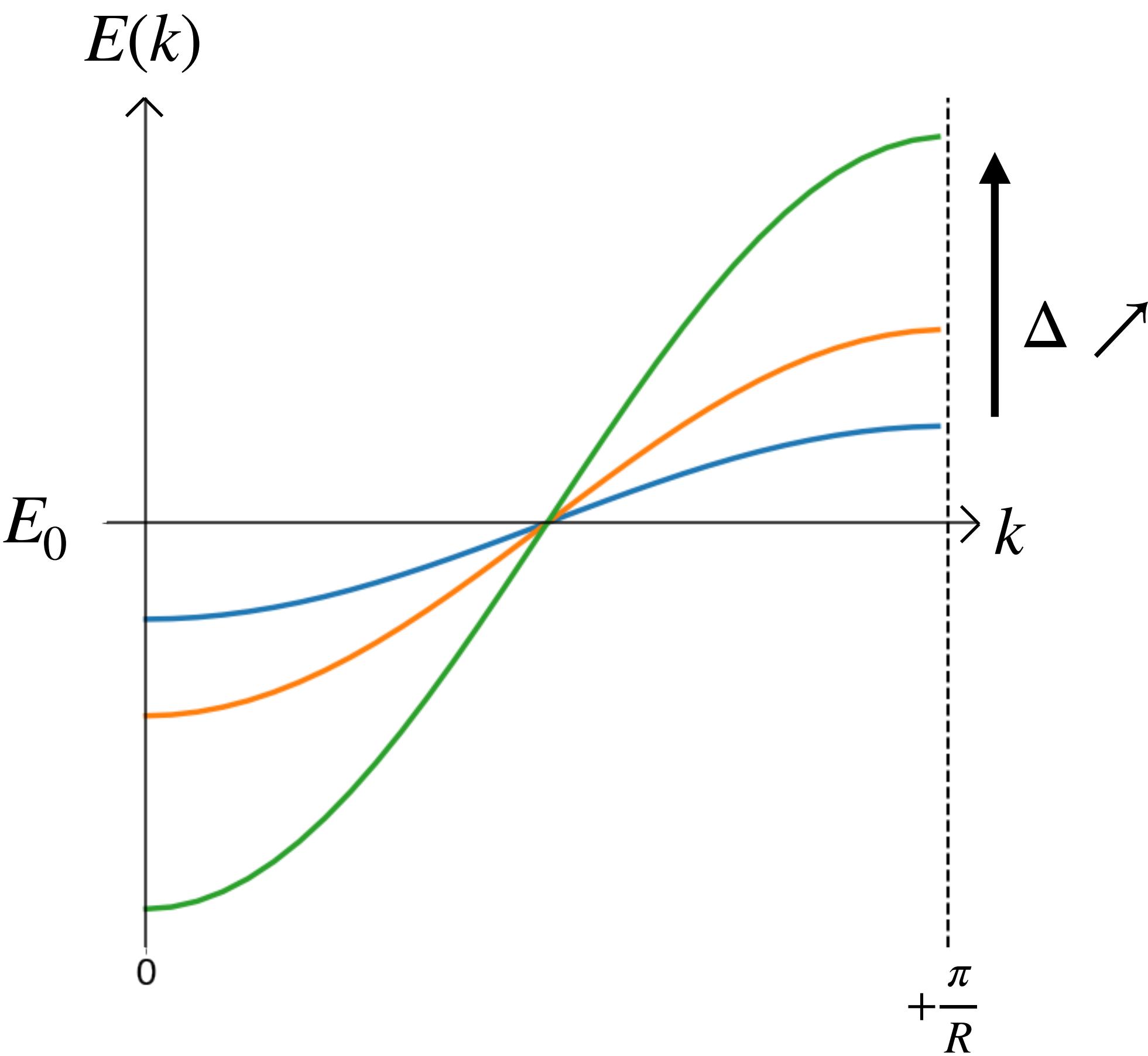
$$\langle k | \hat{H} | k \rangle = \frac{1}{N} \sum_n \langle n | \hat{H} | n \rangle + \frac{1}{N} \sum_n \langle n - 1 | \hat{H} | n \rangle e^{+ikR} + \frac{1}{N} \sum_n \langle n + 1 | \hat{H} | n \rangle e^{-ikR} = E_0 - 2\Delta \cos(kR)$$

For $k = 0$ the energy is $E = E_0 - 2\Delta$ and the state consists of a sum of all atomic orbitals, this can be viewed as a chain of bonding orbitals

For $k = \frac{\pi}{2R}$ the energy is $E = E_0$ and the state consists of a sum of atomic orbitals which are a factor $e^{i\frac{\pi}{2}}$ out of phase, this can be viewed as a chain of non-bonding orbitals

For $k = \frac{\pi}{R}$ the energy is $E = E_0 + 2\Delta$ and the state consists of an alternating sum of atomic orbitals, this can be viewed as a chain of anti-bonding orbitals

One 1D s-band



One 1D s-band

k-space volume of a single state $V_{single\ state} = \frac{\pi}{R}$

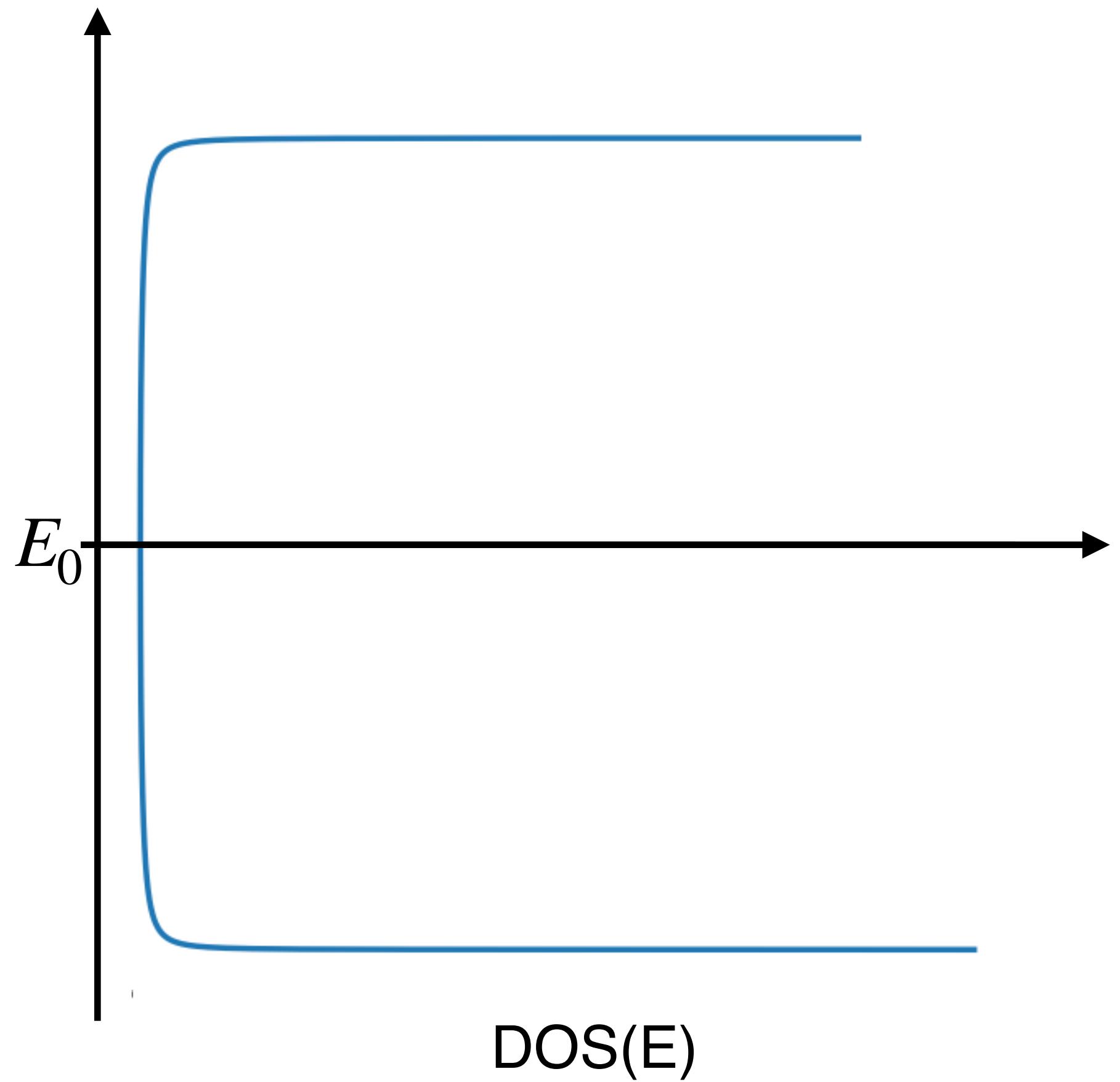
k-space volume occupied by all the states $V_{line} = k$

Number of filled states $N = \frac{V_{line}}{V_{single\ state}} = \frac{kR}{\pi}$

$$\text{DOS}(E) = \frac{1}{V} \frac{dN}{dE} \quad \frac{dN}{dE} = \frac{dN}{dk} \frac{dk}{dE}$$

The DOS is proportional to the inverse of the slope of $E(k)$

The flatter is the band, the greater the DOS is at that energy



Bibliography

Band Theory and Electronic Properties of Solids, John Singleton, Oxford master series in condensed matter physics