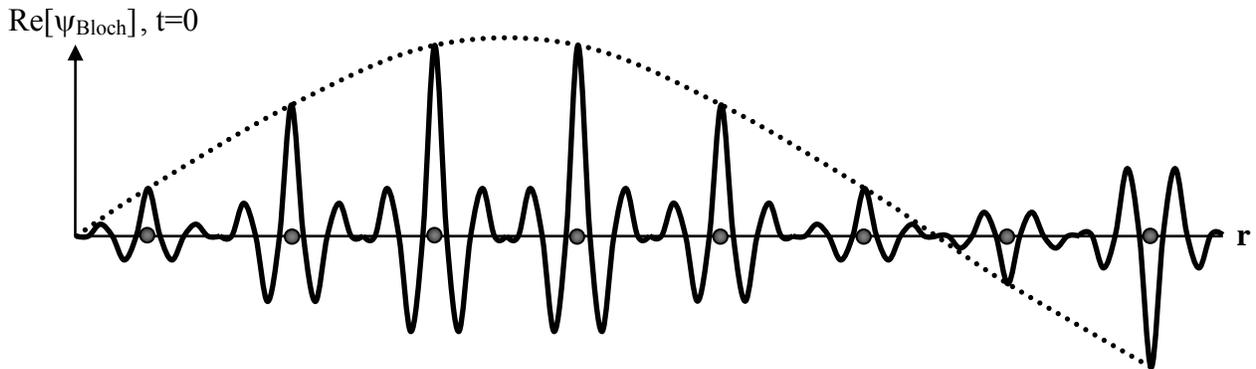


## Electron Waves in a Solid: Bloch Functions

A *Bloch function* combines a plane wave with a periodic sequence of atomic orbitals. The amplitude of the atomic orbitals is modulated by the plane wave (dotted):

$$\psi_{\text{Bloch}}(\mathbf{r}, t) = u_{\mathbf{k}}(\mathbf{r}) \cdot \exp[i(\mathbf{k}\mathbf{r} - \omega t)]$$

$u_{\mathbf{k}}(\mathbf{r})$  is a *periodic function* (for *atomic orbitals*) and  $\exp[i(\mathbf{k}\mathbf{r} - \omega t)]$  a *plane wave* (for *free electrons*). For plots one usually takes the real part of  $\exp$  (which is  $\cos$ ) and sets  $t=0$ .



When a lattice vector  $\mathbf{r}_n$  is added to  $\mathbf{r}$  in a Bloch function, the wave function changes only by the phase factor  $\exp[i(\mathbf{k}\mathbf{r}_n)]$ . The probability density  $|\psi|^2$  remains unchanged, thereby preserving the periodicity:  $|\psi_{\text{Bloch}}|^2(\mathbf{r} + \mathbf{r}_n) = |\psi_{\text{Bloch}}|^2(\mathbf{r})$

Due to its periodicity in all three directions,  $u_{\mathbf{k}}(\mathbf{r})$  can be expanded into a three-dimensional Fourier series, which is summed over the three Miller indices  $h, k, l$  of  $\mathbf{G}$ :

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{G}\mathbf{r})]$$

The corresponding expansion of  $\psi_{\text{Bloch}}$  has  $(\mathbf{k}+\mathbf{G})$  as variable:

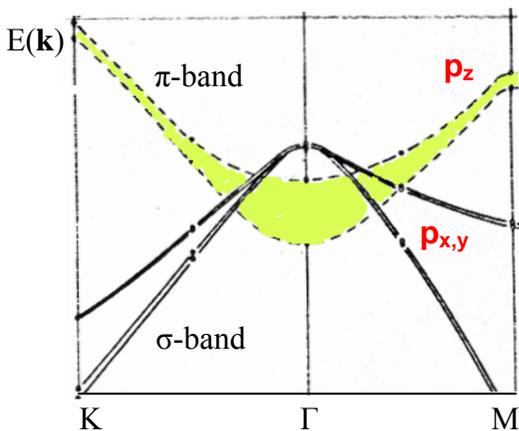
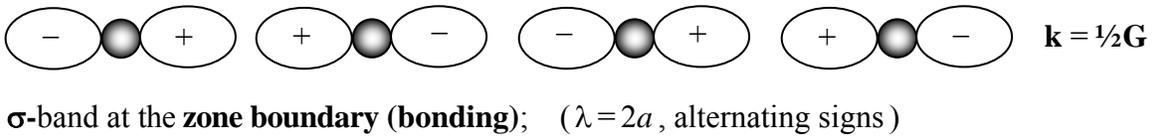
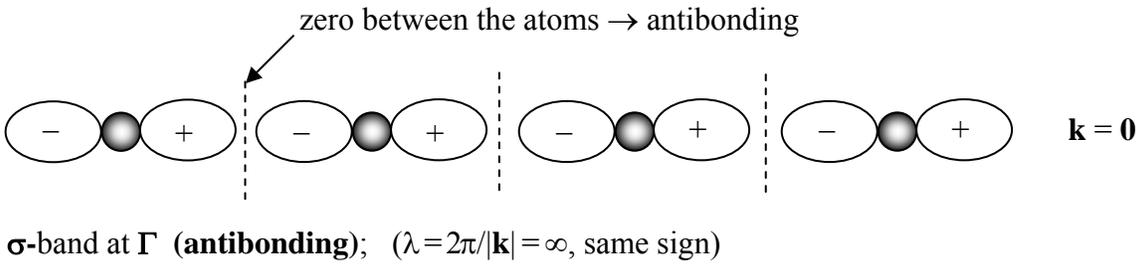
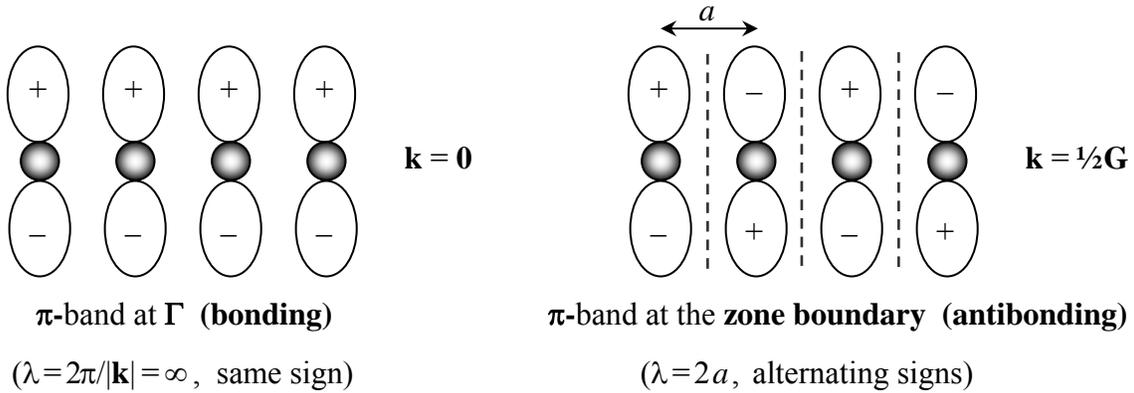
$$\psi_{\text{Bloch}} = \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} \cdot \exp[i[(\mathbf{k}+\mathbf{G})\mathbf{r} - \omega t]]$$

This shows that in a periodic crystal the momentum quantum number  $\mathbf{p} = \hbar\mathbf{k}$  needs to be modified by the substitution:  $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$

This substitution was already used in the diffraction conditions (Lecture 9, Slide 9). The addition of  $\mathbf{G}$  corresponds to a momentum transfer  $\hbar\mathbf{G}$  from the whole crystal. One can make the same substitution in the  $E(\mathbf{k})$  band dispersion:  $E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G})$

$E(\mathbf{k})$  repeats itself in  $\mathbf{k}$ -space, so it is sufficient to know  $E(\mathbf{k})$  inside the Brillouin zone, the unit cell in  $\mathbf{k}$ -space (Lecture 10, Slide 2).

Instead of plotting  $\psi_{\text{Bloch}}$  along a line, one can visualize the atomic orbitals (plotting again their real part, i.e.,  $\cos[\mathbf{k}\mathbf{r}]$  instead of  $\exp[i\mathbf{k}\mathbf{r}]$ ). Consider a row of atoms with p-orbitals oriented either perpendicular or parallel to the  $\mathbf{k}$ -vector. These form  $\pi$ - and  $\sigma$ -bands (compare the notation  $\text{pp}\pi$  and  $\text{pp}\sigma$  on p. 5).



Occupied  $\pi$ - and  $\sigma$ -bands in graphite and graphene: Their bonding vs. antibonding character at the Brillouin zone center  $\Gamma$  and boundary  $K, M$  can be understood the signs of the p-orbitals shown above. (To keep it simple, the  $sp^2$  hybridization and two-dimensional nature of graphene are omitted, plus the fact that there are two C atoms per unit cell.)

## Approximations for E(k)

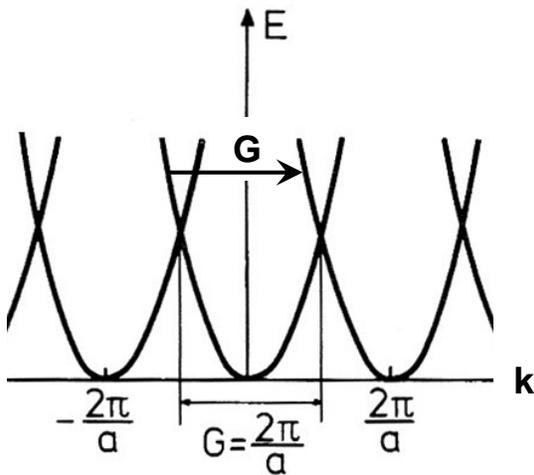
### “Empty Lattice Solution”

These are the bands for a lattice with a constant inner potential  $V_0$ , but no higher Fourier components. Consider only the momentum transfer from the reciprocal lattice vectors  $\mathbf{G}$ . There is no energy change except for  $V_0$ , which corresponds to  $\mathbf{G}=(000)$ .

$$E = \hbar^2/2m_e \cdot (\mathbf{k}+\mathbf{G})^2 + V_0 \approx 3.81 \text{ eV} \cdot (\mathbf{k}+\mathbf{G})^2 \cdot \text{\AA}^2 + V_0 \quad \text{\AA} = 0.1 \text{ nm}$$

Start with  $E = \mathbf{p}^2/2m_e$ , substitute  $\mathbf{p} \rightarrow \hbar\mathbf{k}$ ,  $\mathbf{k} \rightarrow (\mathbf{k}+\mathbf{G})$ , and add the inner potential  $V_0$ .

back-folding = umklapp
 $\approx -15\text{eV}$



#### Empty lattice bands:

The central band is translated by a reciprocal lattice vector  $\mathbf{G}$  (arrow). This leads to an apparent back-folding of the band at the zone boundaries  $\pm \frac{1}{2}\mathbf{G} = \pm \pi/a$ .

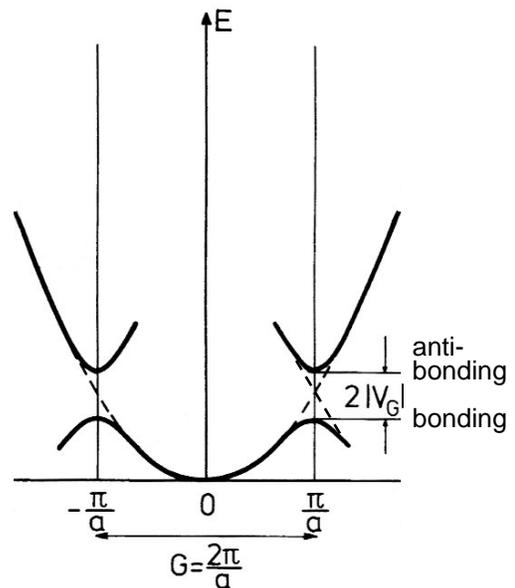
The three-dimensional case is shown in Lect. 17, Slide 2.

### Adding a Periodic Crystal Potential $\Rightarrow$ Band Gaps and Avoided Crossings

A periodic crystal potential  $V(\mathbf{r})$  can be expanded into a Fourier series:

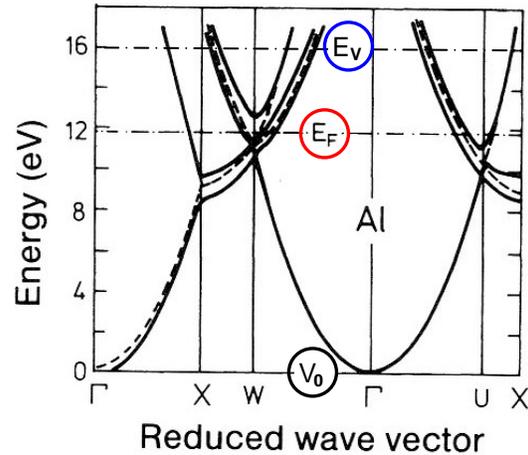
$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \cdot \exp[i(\mathbf{G}\mathbf{r})]$$

$V_{000}$  is the inner potential  $V_0$ . Adding higher Fourier components  $V_{hkl}$  leads to band gaps at the zone boundaries  $\pm \frac{1}{2}\mathbf{G} = \pm \pi/a$ . The size of these gaps is  $2|V_{\mathbf{G}}|$ . Their origin is similar to that of the bonding - antibonding splitting in the  $\text{H}_2$  molecule. Two degenerate energy levels with the same symmetry will always interact with each other in such a way.



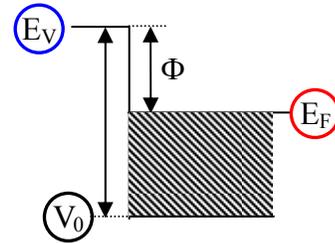
## A Real Band Structure

The band structure of aluminum (full lines) is described rather well by the empty lattice bands (dashed). The main differences are small band gaps at the zone boundaries XW and UX. Therefore, aluminum is often taken as an example for “jellium”, a free electron gas moving in an inner potential  $V_0$  (compare metallic bonding in Lecture 3).

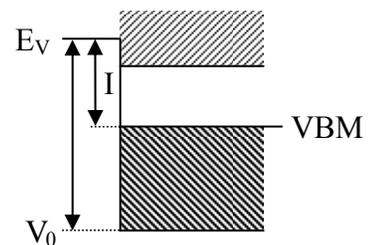


## Two Reference Energies, Two Energy Differences

- 1) The **vacuum level**  $E_V$  is the energy of an electron at rest far from a solid.
- 2) The **Fermi level**  $E_F$  separates filled and empty states.
- 1) The **inner potential**  $V_0$  is the average potential energy of an electron inside a solid, taken relative to  $E_V$  (i.e. negative).
- 2) The **work function**  $\Phi = E_V - E_F$  is the energy to remove an electron from a solid.



In a **semiconductor**, the Fermi level can move around in the gap. Therefore it is useful to replace the Fermi level by the **valence band maximum VBM**, and the work function by the **ionization energy I**.



## Calculation of Electron Energy Bands E(k)

### Localized Electrons (Close to the Atoms): “Tight Binding”

Use interactions between *atomic orbitals* on adjacent atoms, i.e., the factor  $u_k(\mathbf{r})$  of a Bloch function. These are labeled  $ss\sigma$ ,  $pp\pi$ ,  $pp\sigma$ , ... (see the examples on p. 2):

$s, p$  = angular momentum  $l = 0, 1$  of the atomic wave functions (spherical symmetry)

$\sigma, \pi$  = angular momentum  $m = 0, 1$  around the bond axis (axial symmetry)

Input parameters: Interaction energies  $t_1$  and  $t_2$  with the 1<sup>st</sup> and 2<sup>nd</sup> neighbor atoms.

Output:  $E(\mathbf{k})$  has *cosine* form. This happens with *atom-like wave functions*.

Examples: 3d-electrons in noble and transition metals (see Cu, Ni in Lect. 17, p. 3-5).

### Delocalized Electrons (between the Atoms): Plane Waves

Start with the *plane wave expansion* on page 1:  $\psi_{\text{Bloch}} = \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} \cdot \exp[i[(\mathbf{k}+\mathbf{G})\mathbf{r} - \omega t]]$ .

Use only short  $\mathbf{G}$  vectors. Truncate the sum at a maximum  $|\mathbf{G}_{hkl}|$ .

Input parameters: The Fourier coefficients  $V_{hkl}$  of the crystal potential.

Output:  $E(\mathbf{k})$  is approximately *parabolic*, with *gaps* at the *zone boundaries*  $\frac{1}{2}\mathbf{G}_{hkl}$ .

Examples: s,p-electrons in metals (Al, Cu, Ni).

### Universal Method: Density Functional Theory (DFT)

Mainly used in the local density approximation (**LDA**). Reduces the problem from  $10^{23}$  coupled electrons to a single electron in an effective potential. The total electron density  $\rho(\mathbf{r})$  determines everything. It is used widely and free of material-specific parameters.

Total electron density:  $\rho(\mathbf{r}) = \sum_{n,\mathbf{k}} |\psi_{n,\mathbf{k}}|^2$  (n = band number), sum over occupied states

	Kohn-Sham equation: $H \psi_{n,\mathbf{k}} = E_{n,\mathbf{k}} \cdot \psi_{n,\mathbf{k}}$	$H = -\hbar^2/2m_e \cdot \nabla^2 + V_{\text{ion}} + V_C + V_{\text{XC}}$
$V_C$ <span style="font-size: 2em;">{</span>	Potential energy ( $e^-$ - ion attraction):	$V_{\text{ion}} \propto \sum_{\text{ions}} q_i /  \mathbf{r}-\mathbf{r}_i $
	Coulomb energy ( $e^-$ - $e^-$ repulsion):	$V_C(\mathbf{r}) \propto \int \rho(\mathbf{r}') /  \mathbf{r}-\mathbf{r}'  d\mathbf{r}'$
	Exchange-correlation energy:	$V_{\text{XC}}(\mathbf{r}) \propto \rho(\mathbf{r})^{1/3}$

The tricky part is  $V_{\text{XC}}(\mathbf{r})$ , which lumps the complicated many-electron interactions together. It is obtained from the free-electron gas (“jellium”). That works quite well for metals and for the valence band of semiconductors, but the band gap comes out too small.