

BLOCH'S THEOREM

(46) Bloch's theorem identifies the important features of basis functions for the group of lattice translation operations and creates a foundation for solving Schrödinger's equation. For any crystalline solid, the potential energy operator and, therefore, the Hamiltonian operator have the full periodicity of the lattice, i.e., $V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r})$ and $H(\mathbf{r} + \mathbf{T}) = H(\mathbf{r})$, where \mathbf{T} is a Bravais lattice vector. One statement of Bloch's theorem is that the wavefunctions for a particle in such a periodic potential take the form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = A_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

in which $A_{n\mathbf{k}}(\mathbf{r})$ has the full periodicity of the lattice, i.e., $A_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = A_{n\mathbf{k}}(\mathbf{r})$. The functions $\psi_{n\mathbf{k}}(\mathbf{r})$ are modified plane waves. The wavevector \mathbf{k} identifies the IR of the group of lattice translations, and the index n corresponds to any other distinguishing features of the wavefunction, often arising from rotational symmetry. This plane-wave type of wavefunction is best suited for weak crystalline potentials. If the potential energy operator is strong in certain regions of the crystal, then a different expression for these wavefunctions is warranted.

A useful alternative expression of Bloch's theorem concerning $\psi_{n\mathbf{k}}(\mathbf{r})$ is

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(\mathbf{r}).$$

Any function $\psi_{n\mathbf{k}}(\mathbf{r})$ satisfying this equation is called a *Bloch function*. According to this equation, once $\psi_{n\mathbf{k}}(\mathbf{r})$ is known in one unit cell of a crystal, then the function can be immediately evaluated throughout the entire crystal. As a result, calculations of the electronic and vibrational states of crystalline solids can be accomplished by solving the Schrödinger equation for one primitive unit cell.

The second expression of Bloch's theorem is couched in the fundamentals of group theory because Bloch functions are basis functions for the IRs of the group of lattice translations. To show this, the IR labeled by the wavevector \mathbf{k} for the translation operation $(1|\mathbf{T})$ is

$$\Gamma^{(\mathbf{k})}[(1|\mathbf{T})] = e^{-i\mathbf{k}\cdot\mathbf{T}}.$$

If $\psi_{n\mathbf{k}}(\mathbf{r})$ is a basis function for this IR, then

$$(1|\mathbf{T})\psi_{n\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(\mathbf{r}).$$

The effect of the transformation $(1|\mathbf{T})$ on $\psi_{n\mathbf{k}}(\mathbf{r})$ is also (see (38))

$$(1|\mathbf{T})\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n\mathbf{k}}((1|\mathbf{T})^{-1}\mathbf{r}) = \psi_{n\mathbf{k}}((1|-\mathbf{T})\mathbf{r}) = \psi_{n\mathbf{k}}(\mathbf{r} - \mathbf{T}),$$

Therefore,

$$\psi_{n\mathbf{k}}(\mathbf{r} - \mathbf{T}) = e^{-i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(\mathbf{r}) \quad \text{or} \quad \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(\mathbf{r} - \mathbf{T}).$$

If \mathbf{r} is replaced by $\mathbf{r} + \mathbf{T}$, then the second expression of Bloch's theorem is obtained.

(47) The First Brillouin Zone: There are two important corollaries of Bloch's theorem that will be important for solving the Schrödinger equation for electronic and vibrational states in crystals:

- (1) If \mathbf{K} is a reciprocal lattice vector, then the Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r})$ and $\psi_{n(\mathbf{k}+\mathbf{K})}(\mathbf{r})$ are basis functions for the same IR $\Gamma^{(\mathbf{k})}$. That is, these functions are transformed identically by the same lattice translation. Consider each of these two Bloch functions evaluated at $\mathbf{r} + \mathbf{T}$:

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(\mathbf{r}) \quad \text{and}$$

$$\psi_{n(\mathbf{k}+\mathbf{K})}(\mathbf{r} + \mathbf{T}) = e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{T}}\psi_{n(\mathbf{k}+\mathbf{K})}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{T}}e^{i\mathbf{K}\cdot\mathbf{T}}\psi_{n(\mathbf{k}+\mathbf{K})}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{n(\mathbf{k}+\mathbf{K})}(\mathbf{r}).$$

Therefore, $\psi_{n\mathbf{k}}(\mathbf{r})$ and $\psi_{n(\mathbf{k}+\mathbf{K})}(\mathbf{r})$ show the same change in phase factor when \mathbf{r} is shifted to $\mathbf{r} + \mathbf{T}$. Nevertheless, these two functions are distinct basis functions for the same IR $\Gamma(\mathbf{k})$.

- (2) The Bloch function $\psi_{n(-\mathbf{k})}(\mathbf{r})$ and the complex conjugate function $\psi_{n\mathbf{k}}^*(\mathbf{r})$ are basis functions for the same IR $\Gamma(-\mathbf{k})$, as seen as follows:

$$\psi_{n(-\mathbf{k})}(\mathbf{r} + \mathbf{T}) = e^{i(-\mathbf{k})\cdot\mathbf{T}}\psi_{n(-\mathbf{k})}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{T}}\psi_{n(-\mathbf{k})}(\mathbf{r}), \text{ and}$$

$$\psi_{n\mathbf{k}}^*(\mathbf{r} + \mathbf{T}) = [e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(\mathbf{r})]^* = e^{-i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}^*(\mathbf{r}).$$

Moreover, the IR $\Gamma(-\mathbf{k})$ is complex conjugate to $\Gamma(\mathbf{k})$:

$$\Gamma(\mathbf{k})(1|\mathbf{T}) = e^{-i\mathbf{k}\cdot\mathbf{T}} \text{ and } \Gamma(-\mathbf{k})(1|\mathbf{T}) = e^{-(-\mathbf{k})\cdot\mathbf{T}} = e^{i\mathbf{k}\cdot\mathbf{T}} = [\Gamma(\mathbf{k})(1|\mathbf{T})]^*.$$

It is not necessary that $\psi_{n(-\mathbf{k})}(\mathbf{r}) = \psi_{n\mathbf{k}}^*(\mathbf{r})$. Nevertheless, since $\psi_{n(-\mathbf{k})}(\mathbf{r})$ and $\psi_{n\mathbf{k}}^*(\mathbf{r})$ are basis functions for the same IR $\Gamma(-\mathbf{k})$, $\psi_{n(-\mathbf{k})}(\mathbf{r})$ and $\psi_{n\mathbf{k}}(\mathbf{r})$ are degenerate eigenfunctions of the Hermitian Hamiltonian operator, so that $E_n(-\mathbf{k}) = E_n(\mathbf{k})$.

Before discussing some important ramifications of these corollaries, let's examine Bloch functions for the 1-d lattice using the periodic boundary condition $\mathbf{T}_4 = (1|4\mathbf{a}) \equiv (1|\mathbf{0}) = \mathbf{T}_0$. According to slides (43)-(45), $\Gamma(\mu) = e^{-ik_\mu ma}$ for wavevectors $k_\mu = \frac{\mu}{4}\left(\frac{2\pi}{a}\right)$; $\mu = 0, 1, 2, 3$:

\mathcal{L}	\mathbf{T}_0	\mathbf{T}_1	\mathbf{T}_2	\mathbf{T}_3	Bloch Function: $\psi_{k_\mu} = e^{ik_\mu x}$ ($A_{k_\mu} = 1$)		
					k_μ (Wavevector)	Real: $\cos k_\mu x$	Imaginary: $\sin k_\mu x$
$\Gamma^{(0)}$	+1	+1	+1	+1	$k_0 = \frac{0}{4}\left(\frac{2\pi}{a}\right) = 0$		
					$k_4 \equiv k_0 + K_1 = \frac{2\pi}{a}$		
$\Gamma^{(1)}$	+1	-i	-1	+i	$k_1 = \frac{1}{4}\left(\frac{2\pi}{a}\right) = \frac{\pi}{2a}$		
$\Gamma^{(2)}$	+1	-1	+1	-1	$k_2 = \frac{2}{4}\left(\frac{2\pi}{a}\right) = \frac{\pi}{a}$		
$\Gamma^{(3)}$	+1	+i	-1	-i	$k_3 = \frac{3}{4}\left(\frac{2\pi}{a}\right) = \frac{3\pi}{2a}$		
					$k_{-1} \equiv k_3 - K_1 = \frac{-\pi}{2a}$		

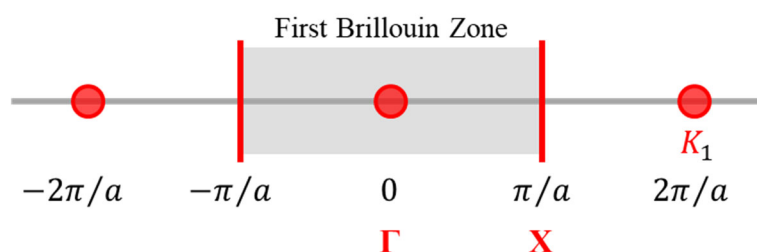
0 a 2a 3a 4a 0 a 2a 3a 4a

Some outcomes of this table include

- The Bloch functions $\psi_{k_0}(x)$ and $\psi_{k_0+K_1}(x)$ where $K_1 = 2\pi/a$ are distinct basis functions for the IR $\Gamma^{(0)}$. Since $k_0 + K_1 = 2\pi/a$, we can write $k_0 + K_1 \equiv k_4$.
- The Bloch functions $\psi_{k_3}(x)$ and $\psi_{k_3-K_1}(x)$ where $K_1 = 2\pi/a$ are distinct basis functions for the IR $\Gamma^{(3)}$. Since $k_3 - K_1 = -\pi/2a$, we can write $k_3 - K_1 \equiv k_{-1}$.
- $\Gamma^{(1)}$ and $\Gamma^{(3)}$ are complex conjugate IRs; the basis functions, $\psi_{k_3}(x)$ and $\psi_{k_{-1}}(x)$, are complex conjugates of each other.

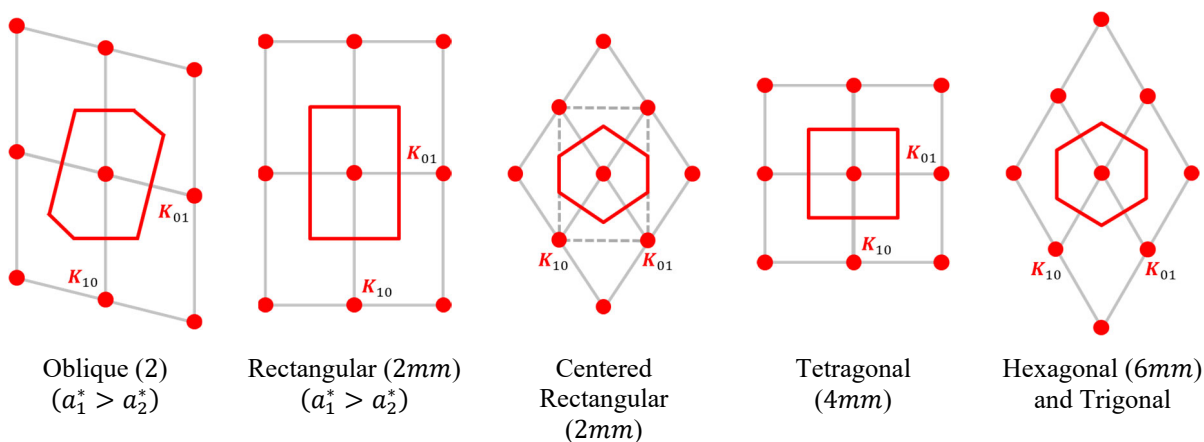
Bloch's theorem and its corollaries indicate that the wavevectors that label the IRs of the group of lattice translations fall within any single unit cell of the reciprocal lattice. This region, which is chosen to be the Wigner-Seitz cell of the reciprocal lattice point $K_{000} = \mathbf{0}$, is called the *first Brillouin zone*. These regions are illustrated below for various 1-d, 2-d, and 3-d reciprocal lattices.

1-d Lattice (Rotational Symmetry $\bar{1}$):

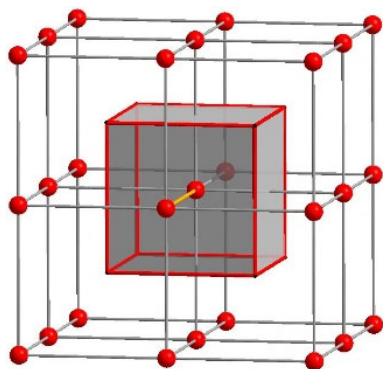
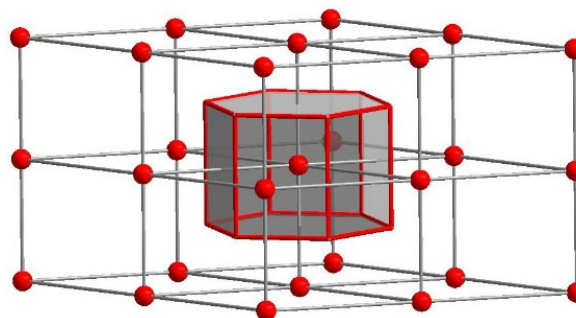
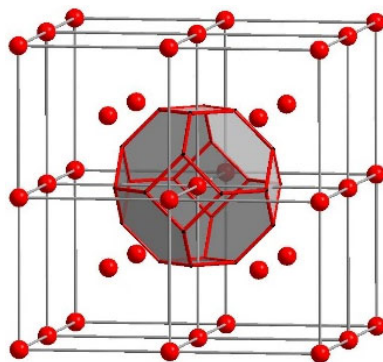
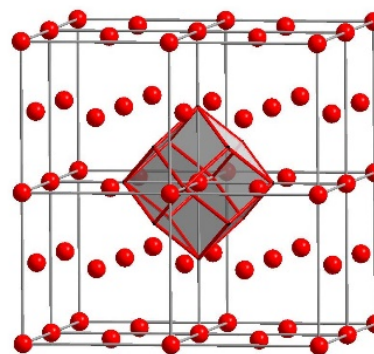


The first Brillouin zone contains wavevectors $-\pi/a < k_\mu \leq \pi/a$. The two boundary points are equivalent because they differ by the reciprocal lattice vector $K_1 = 2\pi/a$. When solving the Schrödinger equation for problems involving 1-d lattices, the second corollary of Bloch's theorem reduces this region to $0 \leq k_\mu \leq \pi/a$, called the *irreducible wedge*. Certain wavevectors get special labels, e.g., $\Gamma = 0$ and $X = \pi/a$.

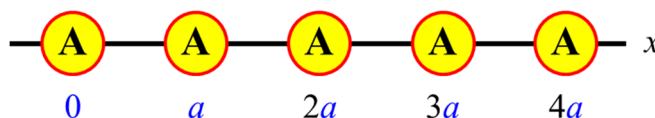
2-d Lattices:



The first Brillouin zones have the full rotational symmetries of their corresponding lattices. Their irreducible wedges, which will be discussed in more detail in the next section, take into account the second corollary as well as rotational symmetry.

Selected 3-d Lattices:Simple Cubic ($m\bar{3}m$)Simple Hexagonal ($6/mmm$; $a_3 < a_1^*$)Body-Centered Cubic ($m\bar{3}m$)Face-Centered Cubic ($m\bar{3}m$)

(48) Bloch Functions for L.C.A.O. Methods: As mentioned in (46), if the crystalline potential is not weak throughout the crystal, then plane waves may not be the best starting point for eigenfunctions of the Schrödinger equation. This is especially true for electronic states in insulating, semiconducting, and transition metal compounds. For these crystalline solids, solutions to the Schrödinger equation use the Tight-Binding or Linear Combination of Atomic Orbitals (L.C.A.O.) approximations. Therefore, it is important to construct Bloch functions using atomic orbitals. We demonstrate how this is accomplished by using a 1-d linear chain of atoms, each separated by a distance a . The atoms sit at lattice points, and the group of 1-d lattice translation operations $\{T_m \equiv (1|ma); m = 0, \dots, N - 1\}$ is the group of the Hamiltonian. The periodic boundary condition is applied to N atoms (lattice points).



We start by selecting valence atomic orbital (AO) as an atomic basis function $\varphi_n(x)$. Then, the *symmetry-adapted linear combination* (SALC) $\psi_{nk}(x)$ of this AO for the wavevector k in the first Brillouin zone can be obtained by using the *projection operator* $P^{(k)}$ for the IR $\Gamma^{(k)}$ of the translation group:

$$P^{(k)} = \frac{1}{\sqrt{N}} \sum_m [\Gamma^{(k)}(1|ma)]^* (1|ma) = \frac{1}{\sqrt{N}} \sum_m [e^{-ikma}]^* (1|ma) = \frac{1}{\sqrt{N}} \sum_m e^{ikma} (1|ma).$$

This operator is a summation over all N translation operators of the lattice group. Thus, $1/\sqrt{N}$ is a normalization factor. Applying $P^{(k)}$ to the AO $\varphi_n(x)$ forms the Bloch function:

$$\psi_{nk}(x) = P^{(k)} \varphi_n(x) = \frac{1}{\sqrt{N}} \sum_m e^{ikma} (1|ma) \varphi_n(x) = \frac{1}{\sqrt{N}} \sum_m e^{ikma} \varphi_n(x - ma).$$

According to this expression, the Bloch function $\psi_{nk}(x)$ is delocalized throughout the entire crystal and, for each lattice step, the phase of the atomic basis function changes by e^{ika} . The Bloch functions for every allowed wavevector k in the first Brillouin zone are mutually orthogonal because they are basis functions for distinct IRs of the translation group. As a result, they are also eigenfunctions for the Hamiltonian operator of this 1-d problem and called *crystal orbitals*.

Now, the expectation value of the Hamiltonian for the Bloch function $\psi_{nk}(x)$ gives the wavevector-dependent energy (eigenvalue) $E_n(k)$:

$$E_n(k) = \langle \psi_{nk} | H | \psi_{nk} \rangle = \frac{1}{N} \sum_{m'} \sum_m e^{ik(m-m')a} \langle \varphi_n(x - m'a) | H | \varphi_n(x - ma) \rangle,$$

which contains Hamiltonian integrals between atomic basis functions at different sites in the 1-d crystal. These integrals can be either calculated via first principles methods or assigned numerical values using some type of (semi)empirical approach. A relatively simple method for calculating electronic structures is Hückel theory, which considers just nearest neighbor orbital interactions. In this approximation, two types of integrals are assigned nonzero values:

$$\text{Coulomb Integrals } (m' = m): \quad \alpha \equiv \langle \varphi_n(x - ma) | H | \varphi_n(x - ma) \rangle;$$

$$\text{Resonance Integrals } (m' = m \pm 1): \quad \beta \equiv \langle \varphi_n(x - (m \pm 1)a) | H | \varphi_n(x - ma) \rangle.$$

Coulomb integrals α are on-site integrals corresponding to the AO energy. They are negative values ($\alpha < 0$) because valence electrons occupying these valence AOs are bound in the free atoms. Resonance integrals (also called hopping or transfer integrals) represent interaction energies between AOs on adjacent sites in the structure. These values can be positive (repulsive) or negative (attractive) depending on the through-space orbital overlap. Another feature of Hückel theory is that the atomic basis functions are set to be spatially orthonormal:

$$S_{m'm} \equiv \langle \varphi_n(x - m'a) | \varphi_n(x - ma) \rangle = \delta_{m'm} \text{ (overlap integral)}^{14}.$$

Using these assignments, the wavevector-dependent energy $E_n(k)$ for the 1-d chain of atoms is

$$E_n(k) = \frac{1}{N} [N\alpha + Ne^{ika}\beta + Ne^{-ika}\beta] = \alpha + 2\beta \cos ka.$$

Since the allowed wavevectors form a quasi-continuous set and $E_n(-k) = E_n(k)$, $E_n(k)$ is a quasi-continuous *energy band* that is plotted for wavevectors $0 \leq k \leq \pi/a$. In the following discussion, we apply these concepts for valence s and p AOs at the atoms. To simplify various mathematical expressions, $\varphi_{nk}(ma)$ is substituted for $\varphi_{nk}(x - ma)$.

(49) Electronic Wavefunctions and Energies in 1-d: At each atomic site, we assign a valence s AO, i.e., $\varphi_n(x) \equiv \varphi_s(x)$, which is a spherically symmetric real function. The Bloch function for wavevector k is:

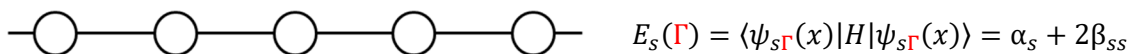
$$\psi_{sk}(x) = \frac{1}{\sqrt{N}} \sum_m e^{ikma} \varphi_s(ma).$$

¹⁴ Resonance integrals are often calculated using overlap integrals, $\beta_{m'm} = H_{m'm} \propto S_{m'm}$. After resonance integrals are determined, then the overlap matrix is set to the identity in Hückel theory.

Now, we examine these Bloch functions and eigenvalues $E_n(k)$ at three wavevectors:

Zone Center $\Gamma, k = 0$:

$$\begin{aligned}\psi_{s\Gamma}(x) &= \frac{1}{\sqrt{N}} \sum_m e^{i0ma} \varphi_s(ma) = \frac{1}{\sqrt{N}} \sum_m (+1)^m \varphi_s(ma) \\ &= \frac{1}{\sqrt{N}} [\varphi_s(0) + \varphi_s(a) + \varphi_s(2a) + \varphi_s(3a) + \varphi_s(4a) \cdots + \varphi_s((N-1)a)]:\end{aligned}$$

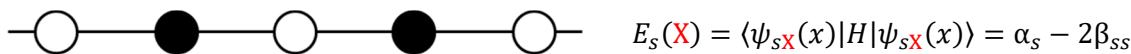


$$E_s(\Gamma) = \langle \psi_{s\Gamma}(x) | H | \psi_{s\Gamma}(x) \rangle = \alpha_s + 2\beta_{ss}$$

The open circles represent $+\varphi_s(x)$. This wavefunction has the *complete translational symmetry* of the structure because there is no phase change in the atomic basis function between adjacent unit cells. As a result, there are no nodes between AOs on adjacent atomic sites. Therefore, this crystal orbital is totally bonding so that $\beta_{ss} < 0$, and it has the lowest energy of the band.

Zone Boundary $X, k = \pi/a$:

$$\begin{aligned}\psi_{sX}(x) &= \frac{1}{\sqrt{N}} \sum_m e^{im\pi} \varphi_s(ma) = \frac{1}{\sqrt{N}} \sum_m (-1)^m \varphi_s(ma) \\ &= \frac{1}{\sqrt{N}} [\varphi_s(0) - \varphi_s(a) + \varphi_s(2a) - \varphi_s(3a) + \varphi_s(4a) \cdots + (-1)^{N-1} \varphi_s((N-1)a)]:\end{aligned}$$



$$E_s(X) = \langle \psi_{sX}(x) | H | \psi_{sX}(x) \rangle = \alpha_s - 2\beta_{ss}$$

The open circles represent $+\varphi_s(x)$; the filled circles represent $-\varphi_s(x)$. Therefore, there are nodes in the wavefunction between every pair of adjacent AOs, and this crystal orbital is totally *antibonding*. It has the highest energy of the band.

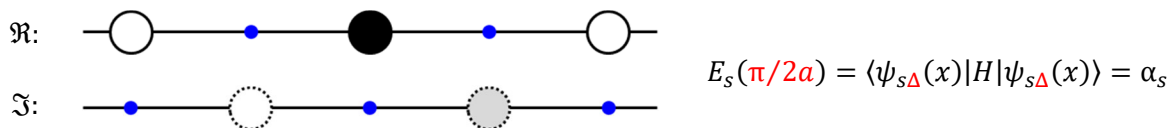
General Point, e.g., $k = \pi/2a$ (all wavevectors $0 < k < \pi/a$ are labelled Δ):

$$\begin{aligned}\psi_{s\Delta}(x) &= \frac{1}{\sqrt{N}} \sum_m e^{im\pi/2} \varphi_s(ma) = \frac{1}{\sqrt{N}} \sum_m (+i)^m \varphi_s(ma) \\ &= \frac{1}{\sqrt{N}} [\varphi_s(0) + i\varphi_s(a) - \varphi_s(2a) - i\varphi_s(3a) + \varphi_s(4a) \cdots + (+i)^{N-1} \varphi_s((N-1)a)]:\end{aligned}$$

This wavefunction is complex with real and imaginary parts:

$$\text{Real Part: } \Re(\psi_{s\Delta}(x)) = \frac{1}{\sqrt{N/2}} [\varphi_s(0) - \varphi_s(2a) + \varphi_s(4a) - \varphi_s(6a) \cdots]:$$

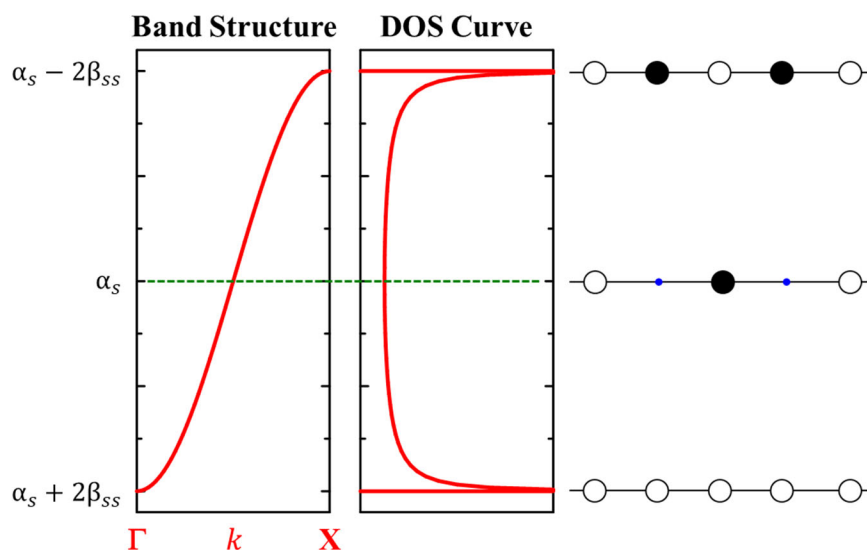
$$\text{Imag. Part: } \Im(\psi_{s\Delta}(x)) = \frac{1}{\sqrt{N/2}} [+i\varphi_s(a) - i\varphi_s(3a) + i\varphi_s(5a) - i\varphi_s(7a) \cdots]:$$



$$E_s(\pi/2a) = \langle \psi_{s\Delta}(x) | H | \psi_{s\Delta}(x) \rangle = \alpha_s$$

In this crystal orbital, real functions alternate with imaginary functions along the lattice. According to the illustrations, both the real and imaginary parts of the Bloch function has nodes at alternating lattice (atomic) sites. Therefore, this wavefunction is *nonbonding* and its eigenvalue is the energy of the s AO.

These results can be summarized in two diagrams:



- The *band structure* illustrates the *s*-band energy as a function of wavevector k from the Brillouin zone center $\Gamma = 0$ to the zone boundary $X = \pi/a$. It is also called an energy dispersion curve. The *s*-band energy increases with increasing wavevector because the crystal orbital at Γ is totally bonding and the crystal orbital at X is totally antibonding. The middle of the energy band is the energy of the atomic *s* AO α_s . The energy difference between the top and bottom of the band is called the *bandwidth*, which is $4|\beta_{ss}|$ in this case. The size of the bandwidth depends on the strength of the orbital interaction between adjacent atomic sites.
- The *DOS curve* shows the relative number of electronic states in a small, fixed energy window plotted as a function of energy. Since each wavevector identifies an eigenfunction and there are N equally spaced wavevectors in the first Brillouin zone ($-\pi/a < k < \pi/a$) arising from the periodic boundary condition, then the density of states in reciprocal space is the total number of states divided by the size (length in 1-d) of the first Brillouin zone, i.e.,

$$\frac{dN(k)}{dk} = \frac{N}{(2\pi/a)} = \frac{Na}{2\pi}.$$

The energy density of states plotted in the DOS curve is the number of states per energy unit:

$$\frac{dN(E)}{dE} = \frac{dN(k)/dk}{|dE(k)/dk|} = \frac{Na}{2\pi} \cdot \frac{1}{2\beta_{ss}a \sin ka} = \frac{N}{4\pi\beta_{ss}} \cdot \frac{1}{\sin ka}.$$

The energy DOS curve is the solid-state analogue of a molecular orbital energy diagram. For the 1-d chain, it shows peaks at the bottom and top and a minimum value at the center $E = \alpha_s$. Integrating the entire DOS curve gives the total number of states in the first Brillouin zone N . Since each crystal orbital (“state”) can hold 2 electrons (spin up and spin down), then the *s*-band in the first Brillouin zone can hold at most $2N$ electrons or 2 electrons per unit cell in real space. Therefore, the number of energy bands in the band structure corresponds to the number of AO basis functions in a single unit cell.

If the chain consists of H atoms, each atom has 1 valence electron and the entire chain after applying the periodic boundary condition has N valence electrons. As a result, only $N/2$ crystal

orbitals of the chain are occupied, which means that the *highest occupied* crystal orbital has $k = \pi/2a$ or $E_s(k) = \alpha_s$. In this case, the wavevector $k = \pi/2a$ is called the *Fermi wavevector* k_F and the corresponding energy $E_s(k_F) \equiv E_F$ is called the *Fermi energy* or *Fermi level*.

(50) We repeat the determination of Bloch functions for p AOs on each atomic site, an exercise that demonstrates how band dispersion is related to the nodal characteristics of the AOs. One of the p AOs is directed along the chain direction and engages in σ -type overlap (p_x), while the other two p AOs are oriented perpendicular to the chain and engage in π -type overlap (p_y, p_z). Since these three AOs are mutually orthogonal, the resulting crystal orbitals are also mutually orthogonal, and the eigenfunctions of the Hamiltonian are the Bloch functions:

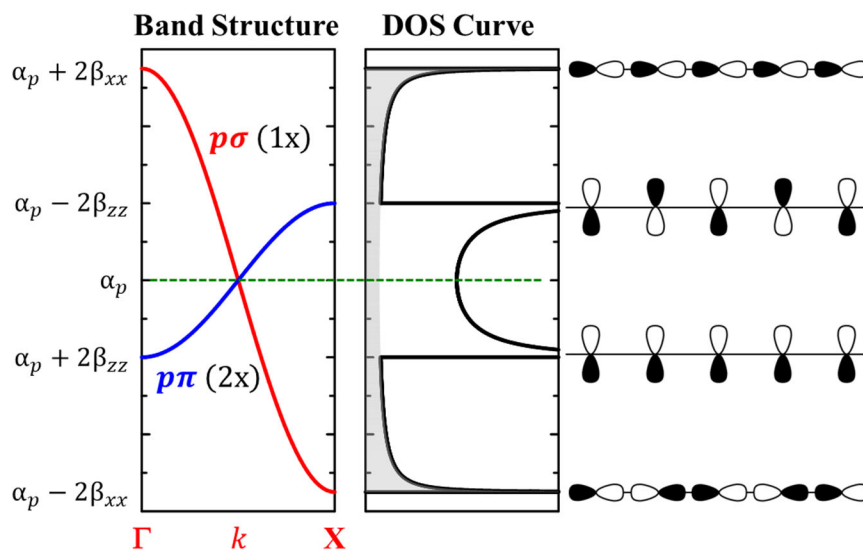
$$\psi_{p_j k}(x) = \frac{1}{\sqrt{N}} \sum_m e^{ikma} \varphi_{p_j}(ma); \quad j = x, y, z.$$

The corresponding wavevector-dependent energies (eigenvalues) are

$$p\sigma \text{ band:} \quad E_{p_x}(k) = \alpha_p + 2\beta_{xx} \cos ka \quad \text{and}$$

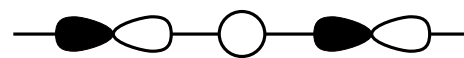
$$p\pi \text{ bands:} \quad E_{p_y}(k) = \alpha_p + 2\beta_{yy} \cos ka = E_{p_z}(k) = \alpha_p + 2\beta_{zz} \cos ka.$$

These results are summarized in the following band structure and DOS curve:



The band structure contains one $p\sigma$ band intersecting two degenerate $p\pi$ bands. This effect in the band structure, called a *symmetry-allowed crossing*, occurs because the p AOs have different rotational symmetry characteristics with respect to the chain direction. Furthermore, the nodal characteristics of the p AOs lead to $\beta_{xx} > 0$ and $\beta_{yy} = \beta_{zz} < 0$. Therefore, the $p\sigma$ Bloch function $\psi_{p_x k}(x)$ at the zone center $k = 0$ is totally antibonding because a positive lobe on one atomic site overlaps with a negative lobe on an adjacent site. Likewise, $\psi_{p_x k}(x)$ at the zone boundary is totally bonding. Therefore, the $p\sigma$ -band decreases in energy from $k = 0$ to π/a . On the other hand, the $p\pi$ -bands increase in energy from the zone center to the zone boundary, just like the s -band. The band center of all bands is the energy of the p AOs α_p , and the bandwidth of the $p\sigma$ -band exceeds that of the $p\pi$ -bands: $4|\beta_{xx}| > 4|\beta_{zz}|$. Thus, the entire DOS curve shows 4 distinct peaks and can accommodate up to 6 electrons per unit cell.

Combining s - and p -Bands: Realistic band structures become complicated as the number of basis AOs in the unit cell increases. With this greater complexity, interactions can arise between different Bloch functions. To demonstrate this effect, consider the 1-d chain of atoms using s and p AOs as the atomic basis functions. These 4 AOs are mutually orthogonal on each atomic site, but there is an additional nearest neighbor σ -interaction between s and p_x AOs (see figure to the right). With a basis set of 4 Bloch functions, the Hamiltonian $H(\mathbf{k})$ is a 4×4 matrix. The diagonal elements are the expressions for the s -, $p\sigma$ -, and two $p\pi$ -bands, and there is one off-diagonal element between the s and p_x AOs:



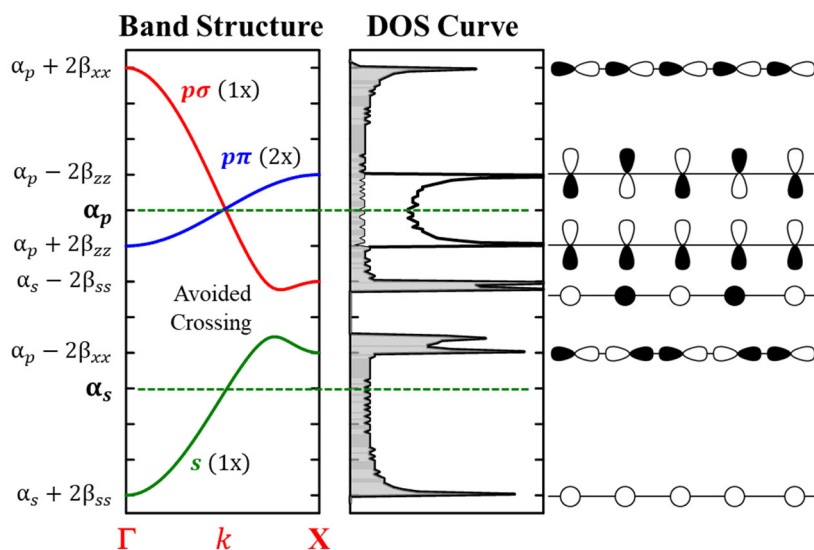
Nature of s - p_x σ -overlap between nearest neighbor atomic sites.

$$\begin{aligned} \langle \psi_{s\mathbf{k}}(x) | H | \psi_{p_x\mathbf{k}}(x) \rangle &= \left\langle \frac{1}{\sqrt{N}} \sum_{m'} e^{ikm'a} \varphi_s(m'a) \middle| H \middle| \frac{1}{\sqrt{N}} \sum_m e^{ikma} \varphi_{p_x}(ma) \right\rangle \\ &= \frac{1}{N} \sum_{m'} \sum_m e^{ika(m-m')} \langle \varphi_s(m'a) | H | \varphi_{p_x}(ma) \rangle \\ &= \frac{1}{N} [N e^{ika} \beta_{sp} - N e^{-ika} \beta_{sp}] = i(2\beta_{sp} \sin ka). \end{aligned}$$

The resulting Hamiltonian matrix that must be diagonalized to give eigenvalues and eigenvectors is

$$H(\mathbf{k}) = \begin{pmatrix} \alpha_s + 2\beta_{ss} \cos ka & i(2\beta_{sx} \sin ka) & 0 & 0 \\ -i(2\beta_{sx} \sin ka) & \alpha_p + 2\beta_{xx} \cos ka & 0 & 0 \\ 0 & 0 & \alpha_p + 2\beta_{yy} \cos ka & 0 \\ 0 & 0 & 0 & \alpha_p + 2\beta_{zz} \cos ka \end{pmatrix},$$

and the results are illustrated in the following band structure and DOS curve:

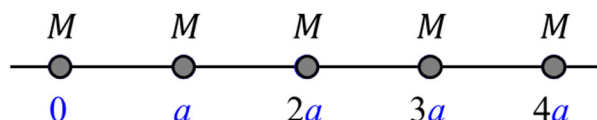


The band structure shows an *avoided crossing* between the s - and $p\sigma$ -bands nearer to the zone boundary X because these two crystal orbitals have identical symmetry characteristics when the wavevector k is between 0 and π/a . According to the off-diagonal Hamiltonian matrix element $H_{sp_x}(\mathbf{k})$, there is no s - $p\sigma$ interaction for $k = 0$ (zone center Γ) and π/a (zone boundary X). Examination of the crystal orbitals at these two points of the band structure indicates that the s - and $p\sigma$ -bands “cross” because the bonding function $\psi_{p_x\mathbf{x}}(x)$ is lower in energy than the antibonding function $\psi_{s\mathbf{x}}(x)$. The two $p\pi$ -bands are orthogonal to the s - and $p\sigma$ -bands.

(51) Vibrational States and Phonon Dispersion Curves: Phonons are vibrational modes of a crystal that form wave packets characterized by a frequency ω and momentum $\hbar\mathbf{k}$. In a solid, they can be created by increasing temperature or providing some mechanical stress. As a result,

phonons are important quasi-particles in solids that contribute to heat conduction and sound propagation. The nature of phonons in crystals are typically investigated by applying the adiabatic approximation, which assumes that nuclear motion does not disturb electronic degrees of freedom and vice versa. This approximation often works because electrons are very much lighter than nuclei so that their velocities are much higher. As a result, electrons adjust essentially immediately to any changes of nuclear positions and nuclear motions are not strongly influenced by electronic motion. Of course, there are characteristics of certain solids where electron-phonon interactions play significant roles, but we will not consider those properties here.

To show the qualitative features of phonons in crystals, we use a 1-dimensional linear chain of atoms of mass M and each pair of atoms separated by interatomic distance a :



The equilibrium positions of each atom are the lattice sites ma . Vibrational motion involves small displacements of the atoms from their equilibrium positions $u_n(ma)$; $n = (x, y, z)$, which are very small movements compared to the interatomic separation a . Three orthogonal displacements yield three distinct phonon modes per atom of the chain. The interatomic potential consists of pairwise interactions that depend only on the interatomic distance $|u_n(ma) - u_n(m'a)|$. Because $u_n(ma)$ are small, this potential can be expanded in a Taylor series. Relative to the potential energy of the equilibrium structure and keeping terms up to second order, this potential takes form

$$\frac{1}{2} K_{mm'} (u_n(ma) - u_n(m'a))^2,$$

in which K_{mn} is the *force constant* between sites ma and $m'a$. The resulting potential energy for the atom at ma is the sum of all pairwise potentials from other atoms in the chain:

$$V_n(ma) = \frac{1}{2} \sum_{m'} K_{mm'} (u_n(ma) - u_n(m'a))^2.$$

Now, if just nearest neighbor interactions in the potential are considered, then the expression is

$$V_n(ma) = \frac{1}{2} K_{\text{vib}} \left[(u_n(ma) - u_n((m+1)a))^2 + (u_n(ma) - u_n((m-1)a))^2 \right].$$

Using this potential, the goal is to evaluate the vibrational frequencies ω_n , which is accomplished by solving Newton's equation of motion for the displacement at each site ma :

$$F_n(ma) = M \frac{d^2 u_n(ma)}{dt^2} = - \frac{dV_n(ma)}{du_n(ma)},$$

which is the harmonic restoring force $F_n(ma)$ exerted at the atom at ma in the 1-d chain. To solve this problem, Bloch's theorem is applied to the displacement:

$$u_{nk}(ma) = u_{n0} e^{-i(\omega_n t - kma)} = u_{n0} e^{-i\omega_n t} e^{ikma}; \quad n = x, y, z.$$

Using this Bloch function in both sides of Newton's equation gives

$$\begin{aligned} M \frac{d^2 u_{nk}(ma)}{dt^2} &= -M \omega_n^2 u_{n0} e^{-i\omega_n t} e^{ikma} = -M \omega_n^2 u_{nk}(ma) \text{ and} \\ - \frac{dV_n(ma)}{du_{nk}(ma)} &= -K_{\text{vib}} [2u_{nk}(ma) - u_{nk}((m+1)a) - u_{nk}((m-1)a)] \\ &= -K_{\text{vib}} [2 - e^{ika} - e^{-ika}] u_{nk}(ma) = -K_{\text{vib}} [2 - 2 \cos ka] u_{nk}(ma). \end{aligned}$$

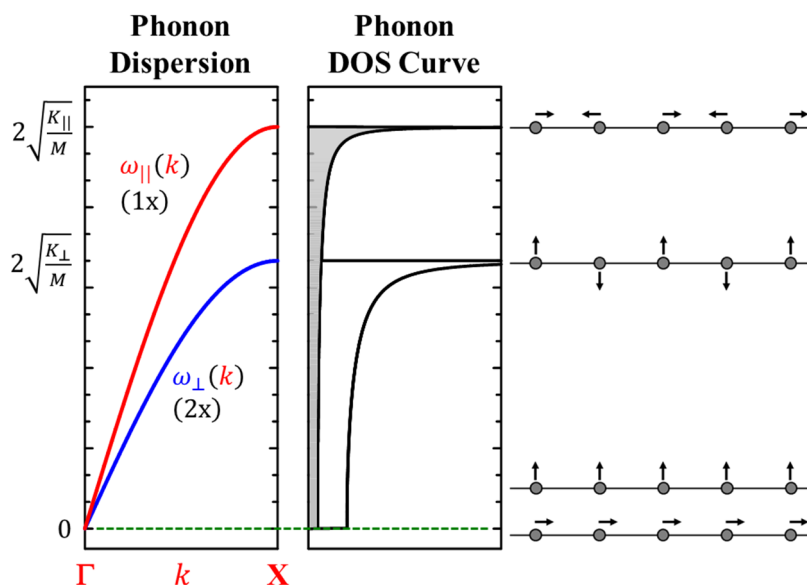
Setting these two expressions equal provides the relationship between phonon frequency and wavevector:

$$\omega_n(k) = 2\sqrt{\frac{K_{\text{vib}}}{M}} \sin \frac{ka}{2}.$$

If the atomic displacements are parallel to the chain $u_{xk}(ma)$, which is assigned to the x -direction, the resulting phonons are called *longitudinal modes*. The force constant is $K_{\text{vib}} \equiv K_{\parallel}$ and these phonons are “stretching”-type vibrations. According to the phonon frequency dispersion relation, the maximum frequency occurs at the zone boundary X : $k = \pi/a$.

(52) If the atomic displacements are perpendicular to the chain $u_{yk}(ma)$ and $u_{zk}(ma)$, the resulting phonons are called *transverse modes*. The force constant is $K_{\text{vib}} \equiv K_{\perp}$ and these phonons are “bending”-type vibrations. Since the force constant for stretching is larger than for bending, $K_{\parallel} > K_{\perp}$, the maximum frequency of the doubly degenerate transverse phonon mode is lower than that for the longitudinal mode.

As for electronic states, the results of these calculations can be plotted in phonon dispersion curves and phonon density of states (DOS):



The phonon dispersion illustrates $\omega_n(k)$ from the zone center Γ ($k = 0$) to the zone boundary X ($k = \pi/a$). The corresponding DOS curve identifies two peaks at the maximum frequencies for stretching and bending phonon modes. In the figures illustrating each phonon mode, the arrows signify the direction and “size” of the atomic displacements, which are, in fact, oscillations about the equilibrium positions of the atoms.

In both dispersion curves, the frequencies $\omega_n(k)$ approach 0 linearly as k approaches 0. At the zone center, all displacements are completely in phase with each other. Therefore, the phonon modes at Γ are *translational modes* because all interatomic distances remain at their equilibrium values. Taking the slope of the phonon dispersion relations as k approaches 0 gives the *speed of sound* for longitudinal and transverse modes in the crystal:

$$\left(\frac{d\omega_{\parallel}}{dk}\right)_{k \rightarrow 0} = \sqrt{\frac{K_{\parallel}a^2}{M}} \quad \text{and} \quad \left(\frac{d\omega_{\perp}}{dk}\right)_{k \rightarrow 0} = \sqrt{\frac{K_{\perp}a^2}{M}}$$

As a result, these three modes are called *acoustic modes* of the crystal.