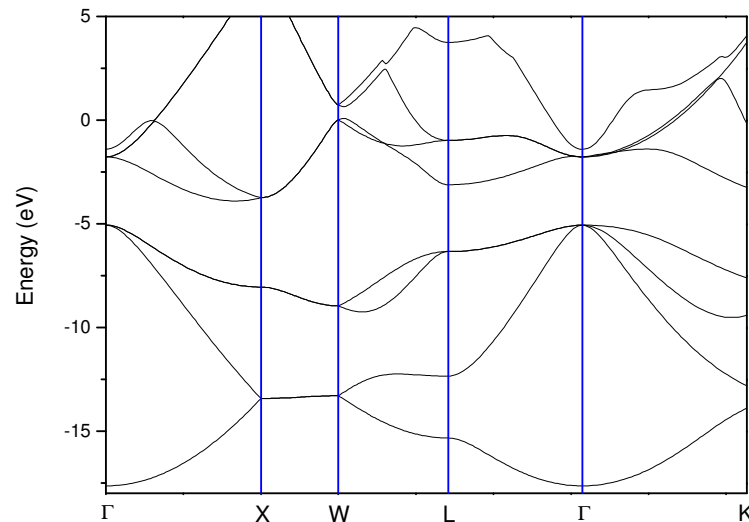# In This Lecture:

➤ **Empirical Pseudopotential Method (EPM)**

➤ **Pseudopotential-based full zone k.p technique**

EPM Bandstructure of Si

Empirical Pseudopotential Method (EPM)

We start with the effective one-electron crystal Hamiltonian

$$H = \frac{p^2}{2m_0} + V_c(\vec{r}); \quad V_c(\vec{r} + \vec{R}) = V_c(\vec{r})$$

Effective xtal potential

A direct lattice vector

Reciprocal lattice vectors

$$\mathcal{H}\psi_{n,\mathbf{k}} = E_{n,\mathbf{k}}\psi_{n,\mathbf{k}}$$

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) u_{\mathbf{G},\mathbf{k}}$$

$$u_{\mathbf{G},\mathbf{k}} = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$
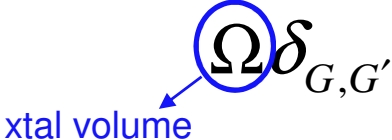
Ref: Harrison

Reciprocal and direct lattice vectors are related by

$$\mathbf{G}\cdot\mathbf{R} = 2\pi n, \quad \text{where} \quad n \in \mathcal{Z} \qquad \text{(to be used soon)}$$

$$\mathcal{H} \sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) u_{\mathbf{G},\mathbf{k}} = E_{n,\mathbf{k}} \sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) u_{\mathbf{G},\mathbf{k}}$$

$$\sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) \mathcal{H} u_{\mathbf{G},\mathbf{k}} = E_{n,\mathbf{k}} \sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) u_{\mathbf{G},\mathbf{k}} \qquad \text{Project this to } u_{\mathbf{G}',\mathbf{k}}$$

$$\sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) \underbrace{\int u_{\mathbf{G}',\mathbf{k}}^{*} \mathcal{H} u_{\mathbf{G},\mathbf{k}} \; d\tau}_{\mathcal{H}_{\mathbf{G}',\mathbf{G}}(\mathbf{k})} = \sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G}) E_{n,\mathbf{k}} \underbrace{\int u_{\mathbf{G}',\mathbf{k}}^{*} u_{\mathbf{G},\mathbf{k}} \; d\tau}_{\Omega \delta_{G,G'}}$$

xtal volume

Ref: Harrison

This results in an eigenvalue equation for <u>each</u> value of **k**:

$$\sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G})\mathcal{H}_{\mathbf{G'},\mathbf{G}} = \sum_{\mathbf{G}} a_{n,\mathbf{k}}(\mathbf{G})E_{n,\mathbf{k}}\delta_{\mathbf{G'},\mathbf{G}}$$

$$\mathcal{H}_{\mathbf{G'},\mathbf{G}}(\mathbf{k})$$

Introduces Energy cut off

This is an infinite set! → Truncate the matrix size within a sphere of RLVs

$$\mathcal{H}_{\mathbf{G'},\mathbf{G}} = \frac{1}{\Omega}\int e^{-i(\mathbf{G'}+\mathbf{k})\bullet\mathbf{r}}\left(-\frac{\hbar^2}{2m_0}\nabla^2\right)e^{i(\mathbf{G}+\mathbf{k})\bullet\mathbf{r}}\ d\tau + \frac{1}{\Omega}\int e^{-i(\mathbf{G'}+\mathbf{k})\bullet\mathbf{r}}\ V_c\ e^{i(\mathbf{G}+\mathbf{k})\bullet\mathbf{r}}\ d\tau$$

xtal volume

$$\mathcal{H}_{\mathbf{G'},\mathbf{G}} = \frac{\hbar^2}{2m_0\Omega}\int |\mathbf{G}+\mathbf{k}|^2 e^{i(\mathbf{G}-\mathbf{G'})\bullet\mathbf{r}}\ d\tau + \frac{1}{\Omega}\int e^{-i(\mathbf{G'}+\mathbf{k})\bullet\mathbf{r}}\ V_c\ e^{i(\mathbf{G}+\mathbf{k})\bullet\mathbf{r}}\ d\tau$$

$$\delta_{\mathbf{G'},\mathbf{G}}$$

V(q): a Fourier xform of xtal potential

Ref: Harrison

Hence, this reveals a <u>diagonal</u> kinetic energy contribution:

$$\mathcal{H}_{\mathbf{G}',\mathbf{G}} = \frac{\hbar^2}{2m_0}|\mathbf{G}+\mathbf{k}|^2\delta_{\mathbf{G},\mathbf{G}'} + V$$

Next, concentrate on the potential term for which we shall insert an atomistic form that is situated at each atomic site $\mathbf{r}_a$:

$$V_c = \sum_{\mathbf{r}_a} V_a(\mathbf{r}-\mathbf{r}_a)$$

$$V = \frac{1}{\Omega}\int e^{-i(\mathbf{G}'+\mathbf{k})\cdot\mathbf{r}}\sum_{\mathbf{r}_a} V_a(\mathbf{r}-\mathbf{r}_a)e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}\ \mathrm{d}\tau$$

$$V = \frac{1}{\Omega}\sum_{\mathbf{r}_a}\int V_a(\mathbf{r}-\mathbf{r}_a)e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}\ \mathrm{d}\tau$$
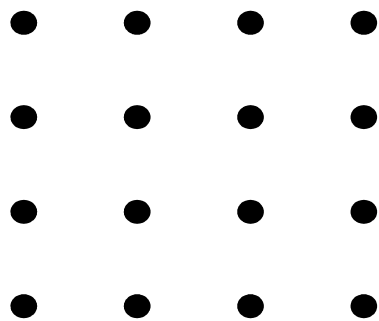
$$\mathbf{r}\longrightarrow\mathbf{r}+\mathbf{r}_a, \qquad V = \frac{1}{\Omega}\sum_{\mathbf{r}_a}\int V_a(\mathbf{r})e^{i(\mathbf{G}-\mathbf{G}')\cdot(\mathbf{r}+\mathbf{r}_a)}\ \mathrm{d}\tau$$

Ref: Harrison

$$V = \frac{1}{\Omega} \sum_{r_a} e^{i(\mathbf{G}-\mathbf{G}')\bullet \mathbf{r}_a} \int V_a(\mathbf{r}) e^{i(\mathbf{G}-\mathbf{G}')\bullet \mathbf{r}} \; d\tau$$

Ref: Harrison

Geometrical (static) structure factor, *S(G-G')*

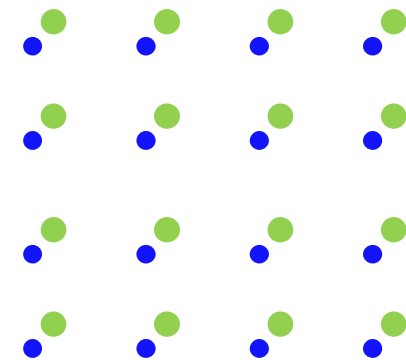Separate $\sum_{r_a}$ into $\sum_{\mathbf{R}} \sum_{\mathbf{t}}$ ⟹ $S = \sum_{\mathbf{R}} \sum_{\mathbf{t}} e^{i(\mathbf{G}-\mathbf{G}')\bullet (\mathbf{R}+\mathbf{t})}$

Direct Lattice (Bravais)

within the basis

basis

lattice

crystal structure

$$S = \sum_{\mathbf{R}} e^{i\overbrace{(\mathbf{G}-\mathbf{G}')}^{\mathbf{G}''}\cdot\mathbf{R}} \sum_{\mathbf{t}} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{t}}$$

$$\underbrace{\mathbf{R}\cdot\mathbf{G}'' = 2\pi n}$$

N : # primitive cells within the computation volume

$$S = N \sum_{\mathbf{t}} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{t}}$$

$$V = \frac{N}{\Omega} \sum_{\mathbf{t}} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{t}} \int V_a(\mathbf{r})e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \, d\tau$$
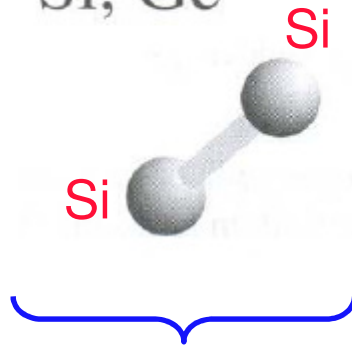
lattice constant

$$N/\Omega = 1/\boxed{\Omega_c} \longrightarrow \text{(primitive) cell volume} \qquad \text{e.g: For FCC lattice} \quad \Omega_c = \frac{A_0^3}{4}$$

Ref: Harrison

Atomic Basis for Diamond & ZB se/c's

Si, Ge

Si

Si

GaAs, InP

As$^+$

Ga$^-$

Diamond: same atoms   Zinc blende: cation-anion
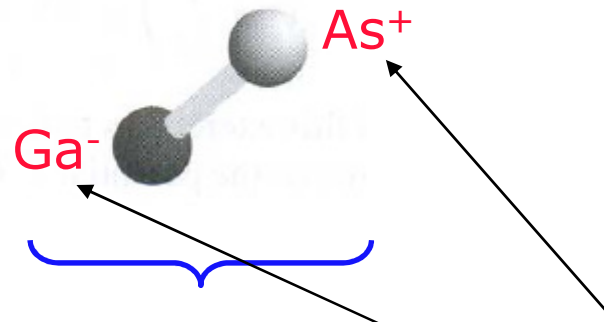
$$\mathbf{t} = \pm\mathbf{T}$$

$$\mathbf{T} = \frac{A_0}{8}(\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}})$$

$$\mathbf{T}^{cat} = -\mathbf{T}, \quad \mathbf{T}^{an} = +\mathbf{T}$$

Ref: Harrison

Pseudopotential Form Factors

$$V = e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{T}} \frac{1}{\Omega_c} \int V_a^{\text{cat}}(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \, d\tau + e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{T}} \frac{1}{\Omega_c} \int V_a^{\text{an}}(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \, d\tau$$

$$\mathbf{q} = \mathbf{G}' - \mathbf{G}$$

$V_f^{\text{cat}}(q)$ Atomic Psp Form Factors $V_f^{\text{an}}(q)$

$$V = \left[V_f^{\text{an}}(q) + V_f^{\text{cat}}(q)\right] \cos(\mathbf{G}-\mathbf{G}')\cdot\mathbf{T} + i\left[V_f^{\text{an}}(q) - V_f^{\text{cat}}(q)\right] \sin(\mathbf{G}-\mathbf{G}')\cdot\mathbf{T}$$

Symmetric Anti-Symm
Psp Form Factors

$$V = V_f^{S}(q) \cos(\mathbf{G}-\mathbf{G}')\cdot\mathbf{T} + iV_f^{A}(q) \sin(\mathbf{G}-\mathbf{G}')\cdot\mathbf{T}$$

Symmetric/Anti-Symm Structure Factors

Ref: Harrison

Here comes the final form of EPM

$$\mathcal{H}_{\mathbf{G'},\mathbf{G}} = \frac{\hbar^2}{2m_0}|\mathbf{G}+\mathbf{k}|^2\delta_{\mathbf{G},\mathbf{G'}} + V_f^S(q)\cos(\mathbf{G}-\mathbf{G'})\boldsymbol{.}\mathbf{T} + iV_f^A(q)\sin(\mathbf{G}-\mathbf{G'})\boldsymbol{.}\mathbf{T}$$

Due to structure factors of Diamond & ZB only few form factors are needed

Form factors are extracted by fitting the b/s to experimental data

Material	A_0 (Å)	$V_f(\sqrt{3})$	$V_f(\sqrt{8})$	$V_f(\sqrt{11})$
Si	5.43	-1.43	$+0.27$	$+0.54$
Ge	5.66	-1.57	$+0.07$	$+0.41$

Material	A_0 (Å)	$V_f^S(q)$			$V_f^A(q)$		
		$\sqrt{3}$	$\sqrt{8}$	$\sqrt{11}$	$\sqrt{3}$	2	$\sqrt{11}$
GaAs	5.64	-3.13	$+0.14$	$+0.82$	$+0.95$	$+0.68$	$+0.14$
InAs	6.04	-2.99	0.00	$+0.68$	$+1.09$	$+0.68$	$+0.41$
GaP	5.44	-2.99	$+0.41$	$+0.95$	$+1.63$	$+0.95$	$+0.27$
InP	5.86	-3.13	$+0.14$	$+0.82$	$+0.95$	$+0.68$	$+0.14$

Ref: Harrison

Sometimes as in strained lattices, form factors are needed over all wave vectors
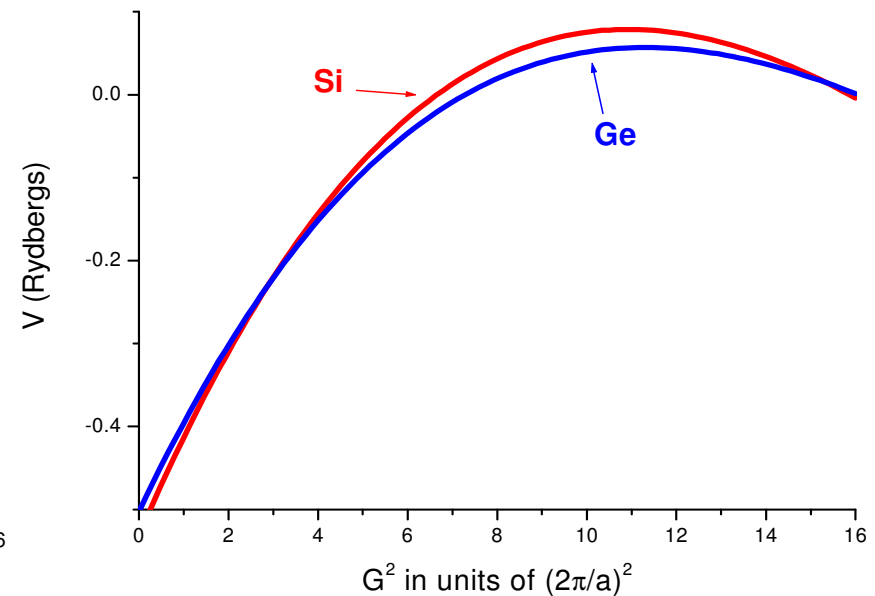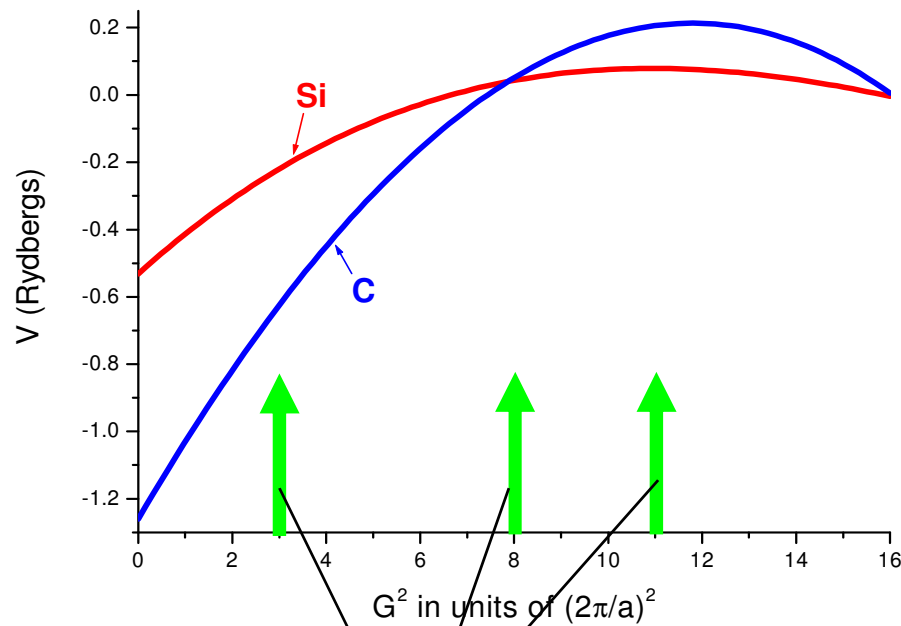
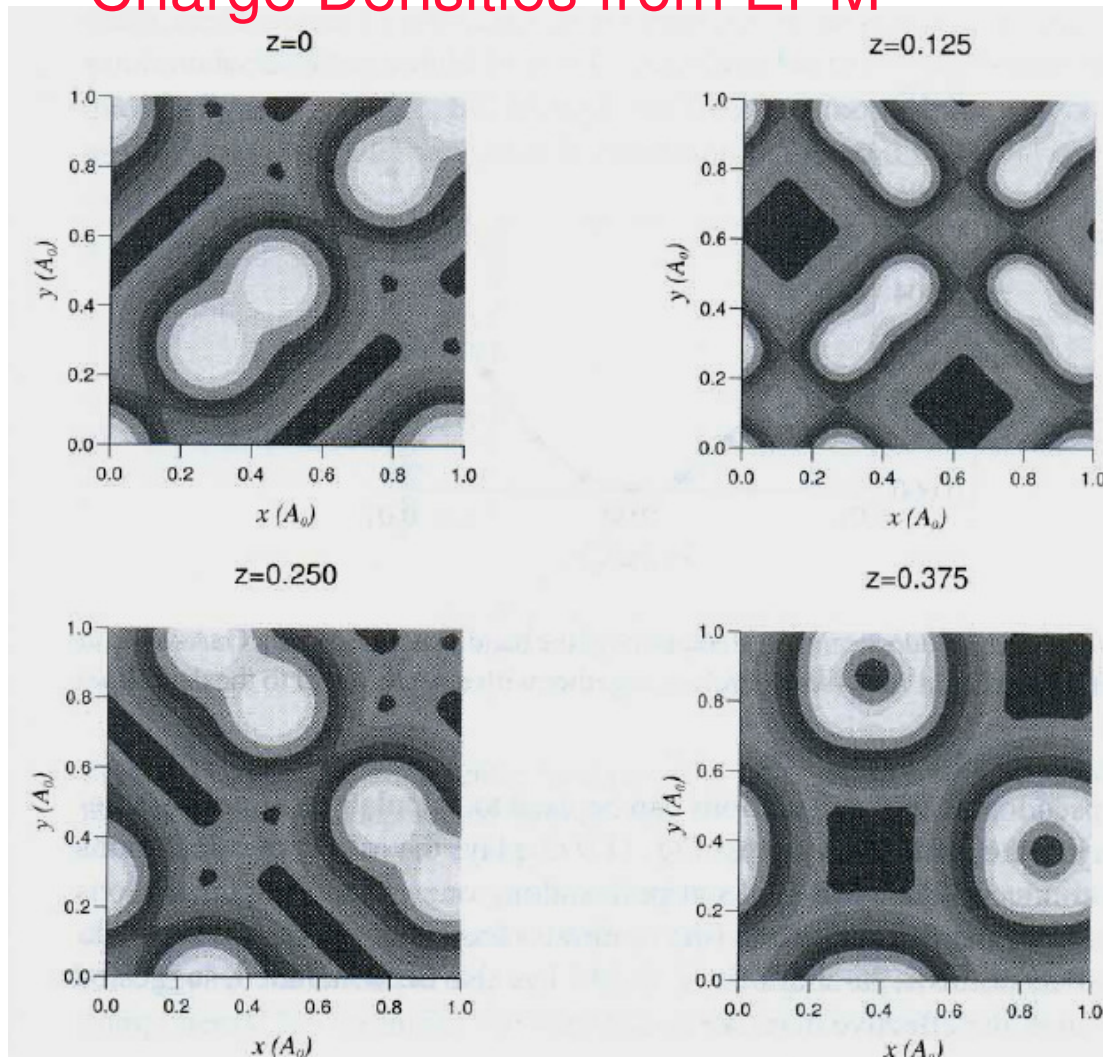Lowest non-vanishing components used for a fixed lattice constant, *a*

Now from symmetric/antisymmetric back to atomic form factors

$$V_f^{an}(q) = \frac{1}{2}\left[V_f^S(q) + V_f^A(q)\right] \qquad V_f^{cat}(q) = \frac{1}{2}\left[V_f^S(q) - V_f^A(q)\right]$$

Cation	Anion	$V_f^{cat}(q)$		$V_f^{an}(q)$	
		$\sqrt{3}$	$\sqrt{11}$	$\sqrt{3}$	$\sqrt{11}$
Ga	As	−2.04	+0.34	−1.09	+0.48
In	As	−2.04	+0.14	−0.95	+0.54
Ga	P	−2.31	+0.34	−0.68	+0.61
In	P	−2.04	+0.34	−1.09	+0.48

Note the change in atomic form factors as extracted from different compound band structures. This brings in the issue of the transferability of the atomic form factors; one partial remedy is non-local EPM

Ref: Harrison

Charge Densities from EPM

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{G}} a_{n,\vec{k}}(\vec{G})\ e^{i(\vec{G}+\vec{k})\cdot\vec{r}}$$

$$\rho(\vec{r}) = \sum_{n,\vec{k}} \psi^*_{n,\vec{k}}(\vec{r})\psi_{n,\vec{k}}(\vec{r})$$

Figure 11.8 Total valence-band charge density for GaAs across the x–y plane of a single face-centred-cubic unit cell, for a variety of z values (given in A_0); note that the lighter the colour, then the higher the charge density. The Bravais lattice points are at the corners and centre of the $z = 0$ plane and on the edges of the $z = 0.5A_0$ plane
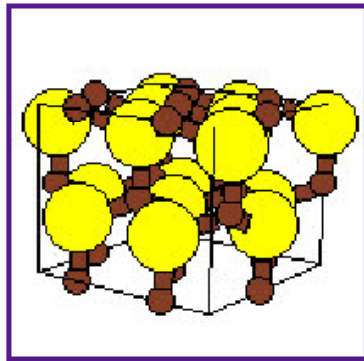
Ref: Harrison

Lowest RLVs in FCC

Table 11.1 The first 65 reciprocal lattice vectors of a face-centred cubic crystal (in units of $2\pi/A_0$)

Direction	Permutations						Magnitude
$\langle 000 \rangle$	$[000]$						0
$\langle 111 \rangle$	$[111]$	$[\bar{1}11]$	$[1\bar{1}1]$	$[11\bar{1}]$	$[\bar{1}\bar{1}1]$	$[1\bar{1}\bar{1}]$	$\sqrt{3}$
	$[\bar{1}1\bar{1}]$	$[\bar{1}\bar{1}\bar{1}]$					
$\langle 200 \rangle$	$[200]$	$[020]$	$[002]$	$[\bar{2}00]$	$[0\bar{2}0]$	$[00\bar{2}]$	2
$\langle 220 \rangle$	$[220]$	$[202]$	$[022]$	$[\bar{2}20]$	$[20\bar{2}]$	$[02\bar{2}]$	$\sqrt{8}$
	$[2\bar{2}0]$	$[\bar{2}02]$	$[0\bar{2}2]$	$[\bar{2}\bar{2}0]$	$[\bar{2}0\bar{2}]$	$[0\bar{2}\bar{2}]$	
$\langle 311 \rangle$	$[311]$	$[131]$	$[113]$	$[\bar{3}11]$	$[\bar{1}31]$	$[\bar{1}13]$	$\sqrt{11}$
	$[3\bar{1}1]$	$[1\bar{3}1]$	$[11\bar{3}]$	$[11\bar{3}]$	$[31\bar{1}]$	$[13\bar{1}]$	
	$[3\bar{1}\bar{1}]$	$[1\bar{3}\bar{1}]$	$[\bar{1}\bar{1}3]$	$[\bar{3}\bar{1}1]$	$[\bar{1}\bar{3}1]$	$[1\bar{1}3]$	
	$[\bar{3}1\bar{1}]$	$[\bar{1}3\bar{1}]$	$[\bar{1}1\bar{1}]$	$[\bar{3}\bar{1}\bar{1}]$	$[\bar{1}\bar{3}\bar{1}]$	$[\bar{1}\bar{1}3]$	
$\langle 222 \rangle$	$[222]$	$[\bar{2}22]$	$[2\bar{2}2]$	$[22\bar{2}]$	$[\bar{2}\bar{2}2]$	$[\bar{2}2\bar{2}]$	$\sqrt{12}$
	$[2\bar{2}\bar{2}]$	$[\bar{2}2\bar{2}]$					
$\langle 400 \rangle$	$[400]$	$[040]$	$[004]$	$[\bar{4}00]$	$[0\bar{4}0]$	$[00\bar{4}]$	4

Ref: Harrison

EPM for the wurtzite structure

The Wurtzite (B4) Structure

- This is the hexagonal analog of the zincblende lattice, i.e. the stacking of the ZnS dimers is ABABAB...
- Replacing both the Zn and S atoms by C (or Si) gives the hexagonal diamond structure.
- The ``ideal'' structure, where the nearest-neighbor environment of each atom is the same as in zincblende, is achieved when we take $c/a = (8/3)^{1/2}$ and $u = 3/8$.
- Note that we have arbitrarily chosen the ``u'' parameter for the Zinc atoms to be zero.

From NRL crystal structure database

- Prototype: ZnS (Wurtzite)
- Pearson Symbol: hP4
- *Strukturbericht* Designation: B4
- Space Group: P6₃mc (Cartesian and lattice coordinate listings available)
- Number: 186
- Other Compounds with this Structure: ZnO, SiC, AlN, CiSe, BN, C(Hexagonal Diamond)
- Primitive Vectors:

$$\mathbf{A_1} = \tfrac{1}{2}\,a\,\mathbf{X} - \tfrac{1}{2}\,3^{1/2}\,a\,\mathbf{Y}$$

$$\mathbf{A_2} = \tfrac{1}{2}\,a\,\mathbf{X} + \tfrac{1}{2}\,3^{1/2}\,a\,\mathbf{Y}$$

$$\mathbf{A_3} = c\,\mathbf{Z}$$

- Basis Vectors:

$$\mathbf{B_1} = 1/3\,\mathbf{A_1} + 2/3\,\mathbf{A_2} = \tfrac{1}{2}\,a\,\mathbf{X} + \tfrac{1}{2}\,3^{-1/2}\,a\,\mathbf{Y} \quad \text{(Zn)} \quad \text{(2b)}$$

$$\mathbf{B_2} = \begin{matrix} 2/3\,\mathbf{A_1} + 1/3\,\mathbf{A_2} + \\ \tfrac{1}{2}\,\mathbf{A_3} \end{matrix} = \begin{matrix} \tfrac{1}{2}\,a\,\mathbf{X} - \tfrac{1}{2}\,3^{-1/2}\,\mathbf{Y} + \tfrac{1}{2} \\ c\,\mathbf{Z} \end{matrix} \quad \text{(Zn)} \quad \text{(2b)}$$

$$\mathbf{B_3} = \begin{matrix} 1/3\,\mathbf{A_1} + 2/3\,\mathbf{A_2} + \\ u\,\mathbf{A_3} \end{matrix} = \begin{matrix} \tfrac{1}{2}\,a\,\mathbf{X} + \tfrac{1}{2}\,3^{-1/2}\,a\,\mathbf{Y} + \\ u\,c\,\mathbf{Z} \end{matrix} \quad \text{(S)} \quad \text{(2b)}$$

$$\mathbf{B_4} = \begin{matrix} 2/3\,\mathbf{A_1} + 1/3\,\mathbf{A_2} + \\ (\tfrac{1}{2} + u)\,\mathbf{A_3} \end{matrix} = \begin{matrix} \tfrac{1}{2}\,a\,\mathbf{X} - \tfrac{1}{2}\,3^{-1/2}\,a\,\mathbf{Y} + \\ (\tfrac{1}{2} + u)\,c\,\mathbf{Z} \end{matrix} \quad \text{(S)} \quad \text{(2b)}$$

For WZ there are four atoms in the basis in contrast to two for ZB. Since the volume per atom is the same, a given volume of reciprocal space for WZ contains approximately twice as many RLVs.

As in the ZB case the psp for WZ can be written as

$$V(G) = S_S(G)\, V_f^S(G) + S_A(G)\, V_f^A(G),$$

$$V_f^S(G) = V_f^{an}(G) + V_f^{cat}(G), \quad V_f^A(G) = V_f^{an}(G) - V_f^{cat}(G),$$

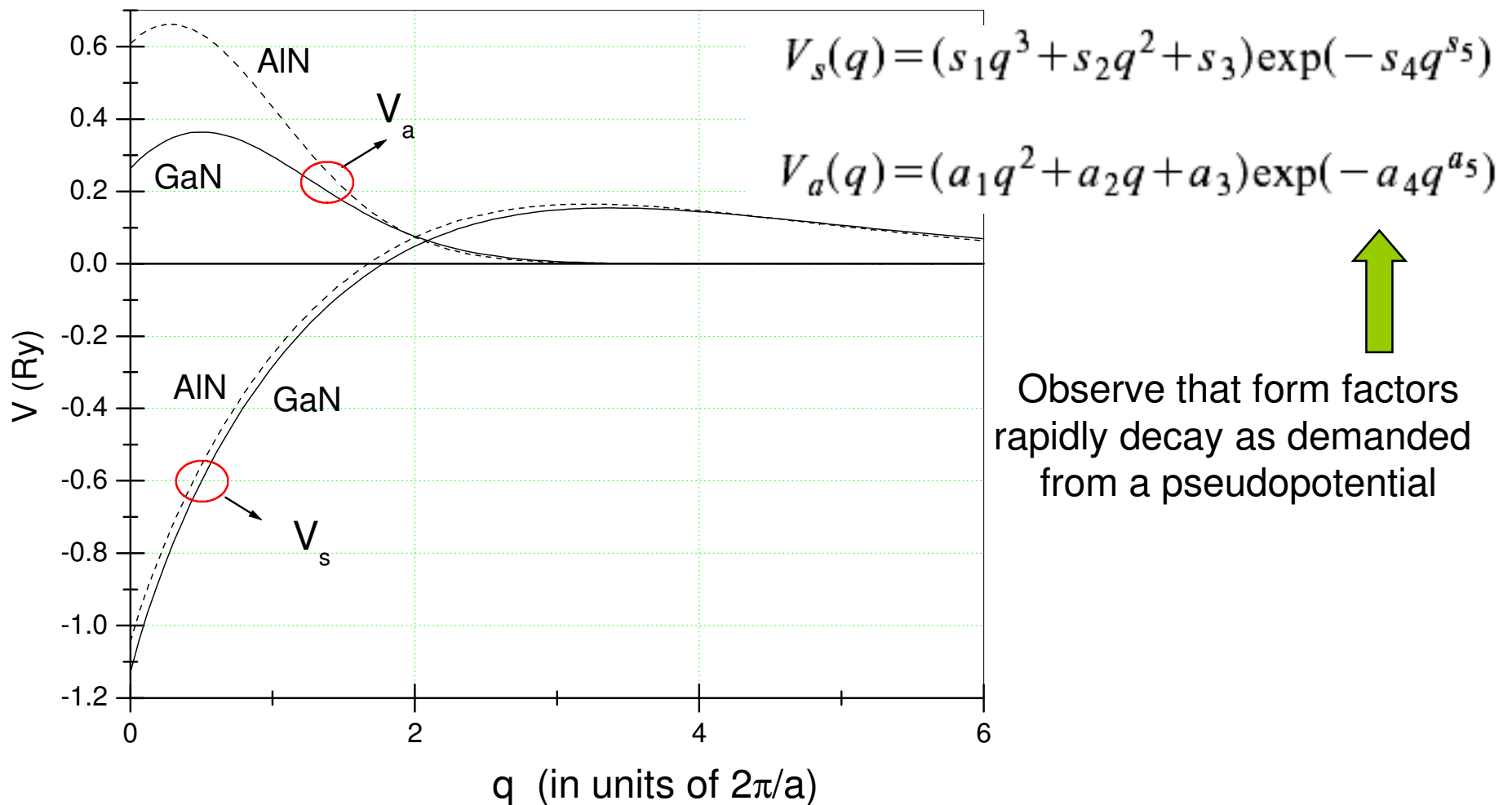$$S_S(G) = \cos\left[2\pi\left(\frac{L}{6} + \frac{M}{6} + \frac{N}{4}\right)\right]\cos(\pi N u),$$

$$S_A(G) = \cos\left[2\pi\left(\frac{L}{6} + \frac{M}{6} + \frac{N}{4}\right)\right]\sin(\pi N u),$$

see prev. page

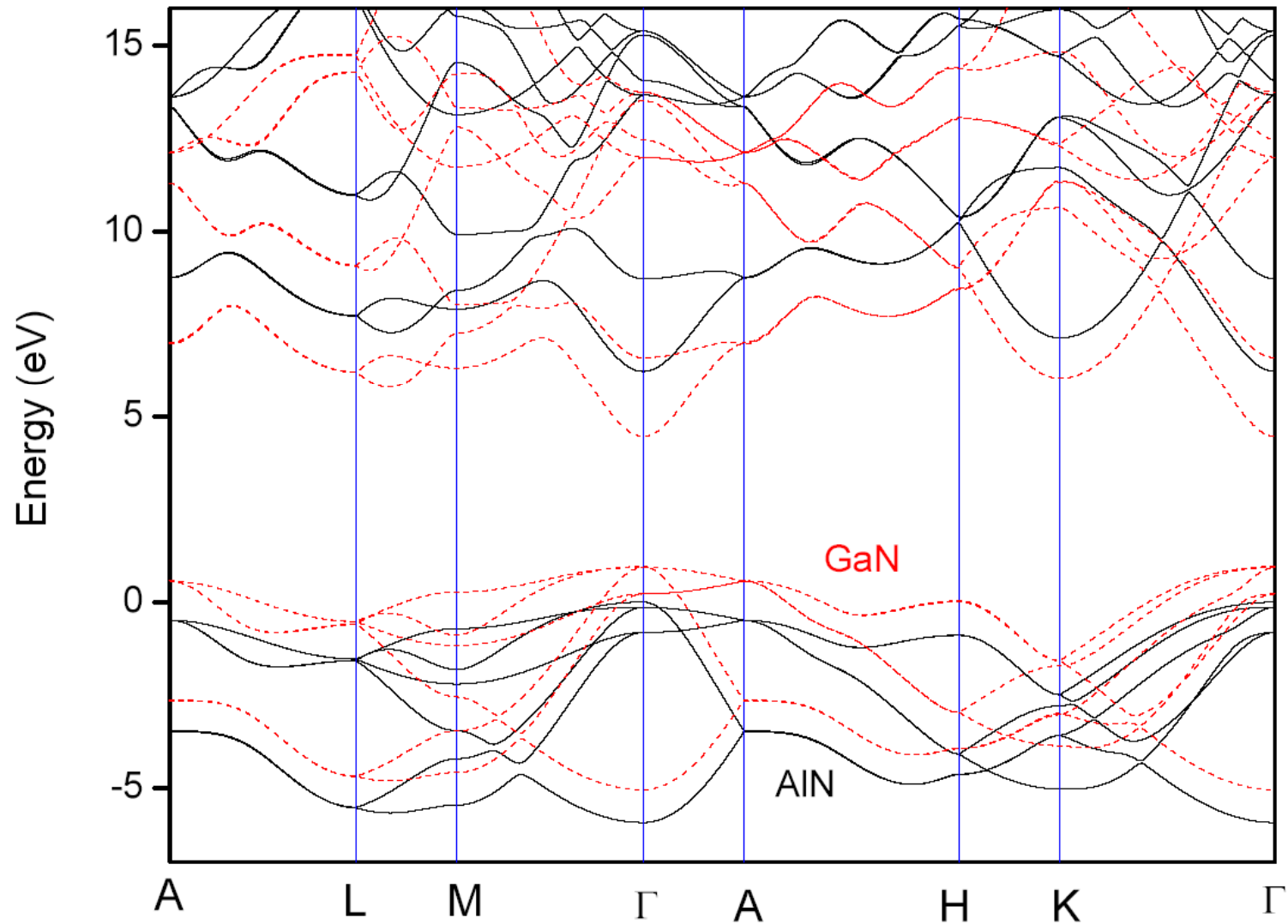$$\text{where } \vec{G} = L\vec{b}_1 + M\vec{b}_2 + N\vec{b}_3$$

Examples on WZ EPM: GaN & AlN

GaN, AlN: EPM Form Factors

$$V_s(q) = (s_1 q^3 + s_2 q^2 + s_3) \exp(-s_4 q^{s_5})$$

$$V_a(q) = (a_1 q^2 + a_2 q + a_3) \exp(-a_4 q^{a_5})$$

Observe that form factors rapidly decay as demanded from a pseudopotential

Examples on WZ EPM: GaN & AlN

Pseudopotential-based full-zone k·p

> 4- or 8-band k·p result in ever-concave-up or down bands [unrealistic away from the band edge]

> In principle, k·p technique becomes <u>exact</u> as the number of bands included goes to infinity

> The problem there lies in proliferation of Luttinger-like parameters which cannot be extracted from experiments

> Wang & Zunger have proposed a pseudopotential based k·p technique where all desired band interaction parameters are taken from ab initio/empirical pseudopotential computations

Formulation

Based on the Reference:
C. Bulutay, Turkish Journal of Physics, **30**, 287 (2006).

Start with the effective one-e Hamiltonian described by a local potential

$$\left[\frac{p^2}{2m_0} + V_{\text{xtal}}(\vec{r})\right]\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n\vec{k}}(\vec{r}), \qquad \psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r}),$$

we obtain the well-known k.p expression in terms of cell-periodic parts

$$\left[H_0 + \frac{\hbar}{m_0}\vec{k}\cdot\vec{p}\right]u_{n\vec{k}}(\vec{r}) = \left[E_n(\vec{k}) - \frac{\hbar^2 k^2}{2m_0}\right]u_{n\vec{k}}(\vec{r}), \quad H_0 = \frac{\hbar^2 k^2}{2m_0} + V_{\text{xtal}}(\vec{r}).$$

Cell-periodic fn's satisfy a Sturm-Liouville type eigenvalue eq. Hence, they are complete when all (infinite) bands are considered at a fixed wv, say k_0

An arbitrary fn, such as $u_{j\vec{k}}(\vec{r})$ can be expanded in terms of this set

$$\left\{ u_{j\vec{k}}(\vec{r}) = \sum_{m=1}^{N_b} b_{j\vec{k},m\vec{k}_0}u_{m\vec{k}_0}(\vec{r}).\right.$$

This leads to the following eigenvalue eq. which becomes exact as $N_b \rightarrow \infty$

$$\sum_{m=1}^{N_b} \left[H_{n\vec{k}_0, m\vec{k}_0}(\vec{k}) - \delta_{nm} E_j(\vec{k}) \right] b_{j\vec{k}, m\vec{k}_0} = 0, \; n \in [1, N_b] \,,$$

where

$$H_{n\vec{k}_0, m\vec{k}_0}(\vec{k}) \equiv \left[E_m(\vec{k}_0) + \frac{\hbar^2}{2m_0} \left(k^2 - k_0^2 \right) \right] \delta_{nm} + \frac{\hbar}{m_0} \left(\vec{k} - \vec{k}_0 \right) \cdot \vec{P}_{n\vec{k}_0, m\vec{k}_0} \,,$$

and $\vec{P}_{n\vec{k}_0, m\vec{k}_0} \equiv \left\langle u_{n\vec{k}_0} \left| \vec{p} \right| u_{m\vec{k}_0} \right\rangle,$ momentum matrix element

Since we cannot include infinite # bands at a fixed wv, we can modify the formulation by forming an expansion basis over <u>various bands</u> and wv, $\{m, \vec{k}_i\}$

$$u_{j\vec{k}}(\vec{r}) = \sum_{\{m, \vec{k}_i\}} b_{j\vec{k}, m\vec{k}_i} u_{m\vec{k}_i}(\vec{r}) \,.$$

Since cell-periodic fn's are not necessariy normal <u>at different wv's</u> we introduce

$$\Delta_{n\vec{k}_s,m\vec{k}_i} \equiv \langle u_{n\vec{k}_s} | u_{m\vec{k}_i} \rangle$$

Then the expansion coefficients satisfy

$$\sum_{\{m,\vec{k}_i\}} \left\{ \left[E_m(\vec{k}_i) - \frac{\hbar^2 k_i^2}{2m_0} \right] + \frac{\hbar}{m_0} \left(\vec{k} - \vec{k}_i \right) \cdot \vec{p} - \left[E_j(\vec{k}) - \frac{\hbar^2 k^2}{2m_0} \right] \right\} b_{j\vec{k},m\vec{k}_i} u_{m\vec{k}_i}(\vec{r}) = 0 \, .$$

Projecting to $|u_{n\vec{k}_s}\rangle$ results in a <u>generalized</u> eigenvalue equation

$$\sum_{\{m,\vec{k}_i\}} \left[H_{n\vec{k}_s,m\vec{k}_i}(\vec{k}) - \Delta_{n\vec{k}_s,m\vec{k}_i} E_j(\vec{k}) \right] b_{j\vec{k},m\vec{k}_i} = 0 \, , \, \forall n, \vec{k}_s \, ,$$

where

$$H_{n\vec{k}_s,m\vec{k}_i}(\vec{k}) \equiv \left[E_m(\vec{k}_i) + \frac{\hbar^2}{2m_0} \left(k^2 - k_i^2 \right) \right] \Delta_{n\vec{k}_s,m\vec{k}_i} + \frac{\hbar}{m_0} \left(\vec{k} - \vec{k}_i \right) \cdot \vec{p}_{n\vec{k}_s,m\vec{k}_i} \, ,$$

$$\vec{p}_{n\vec{k}_s,m\vec{k}_i} \equiv \langle u_{n\vec{k}_s} | \vec{p} | u_{m\vec{k}_i} \rangle \, , \qquad \text{Generalized momentum matrix element linking indirect transitions}$$

So, necessary input for multiband k.p: $E_m(\vec{k}_i)$ $\vec{P}_{n\vec{k}_s,m\vec{k}_i}$ $\Delta_{n\vec{k}_s,m\vec{k}_i}$

These can readily be either extracted or generated from *ab initio* DFT or EPM bandstructure computations:

$$u_{m\vec{k}_i}(\vec{r}) = \frac{1}{\sqrt{\Omega_0}} \sum_{\vec{G}} \boxed{B_{m\vec{k}_i}(\vec{G})} e^{i\vec{G}\cdot\vec{r}}$$

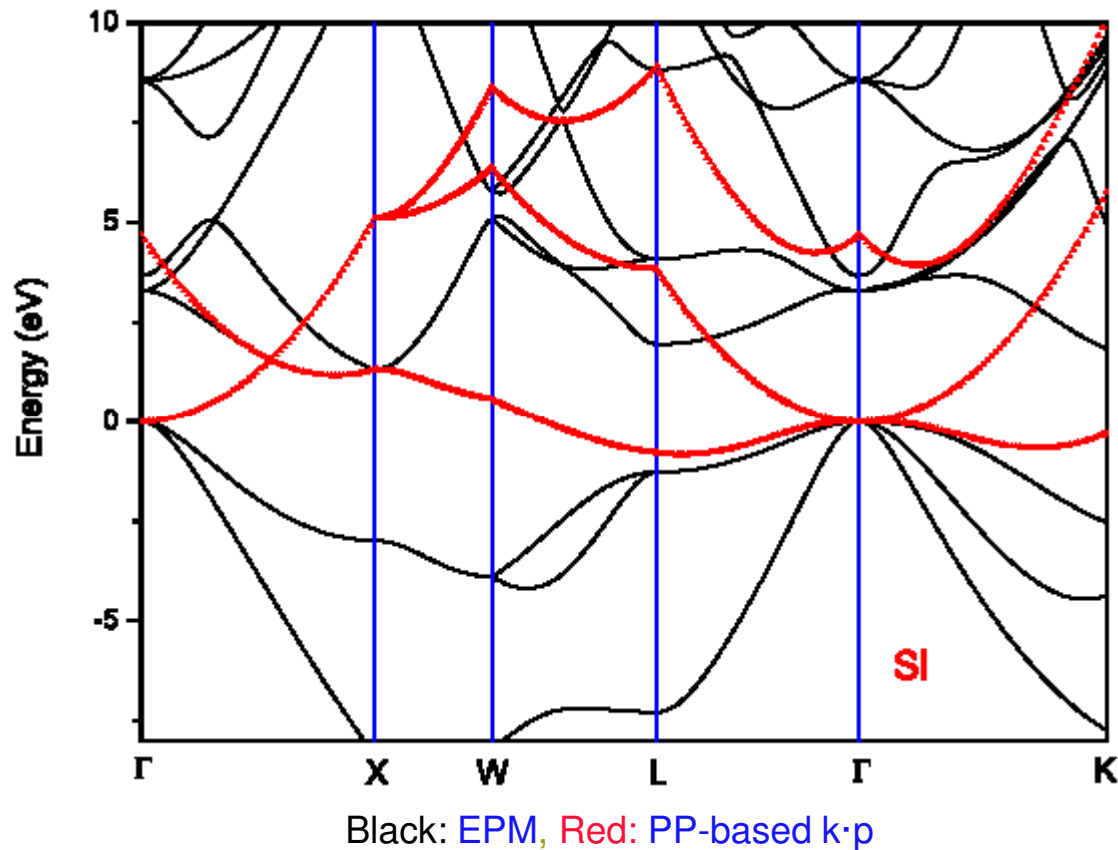eigenvectors obtained from EPM/DFT

Hence ,in terms of these eigenvectors we can generate

$$\Delta_{n\vec{k}_s,m\vec{k}_i} = \sum_{\vec{G}} B^*_{n\vec{k}_s}(\vec{G}) \, B_{m\vec{k}_i}(\vec{G}) \,,$$

$$\vec{P}_{n\vec{k}_s,m\vec{k}_i} = \sum_{\vec{G}} B^*_{n\vec{k}_s}(\vec{G}) \, \hbar\vec{G} \, B_{m\vec{k}_i}(\vec{G}) \,,$$
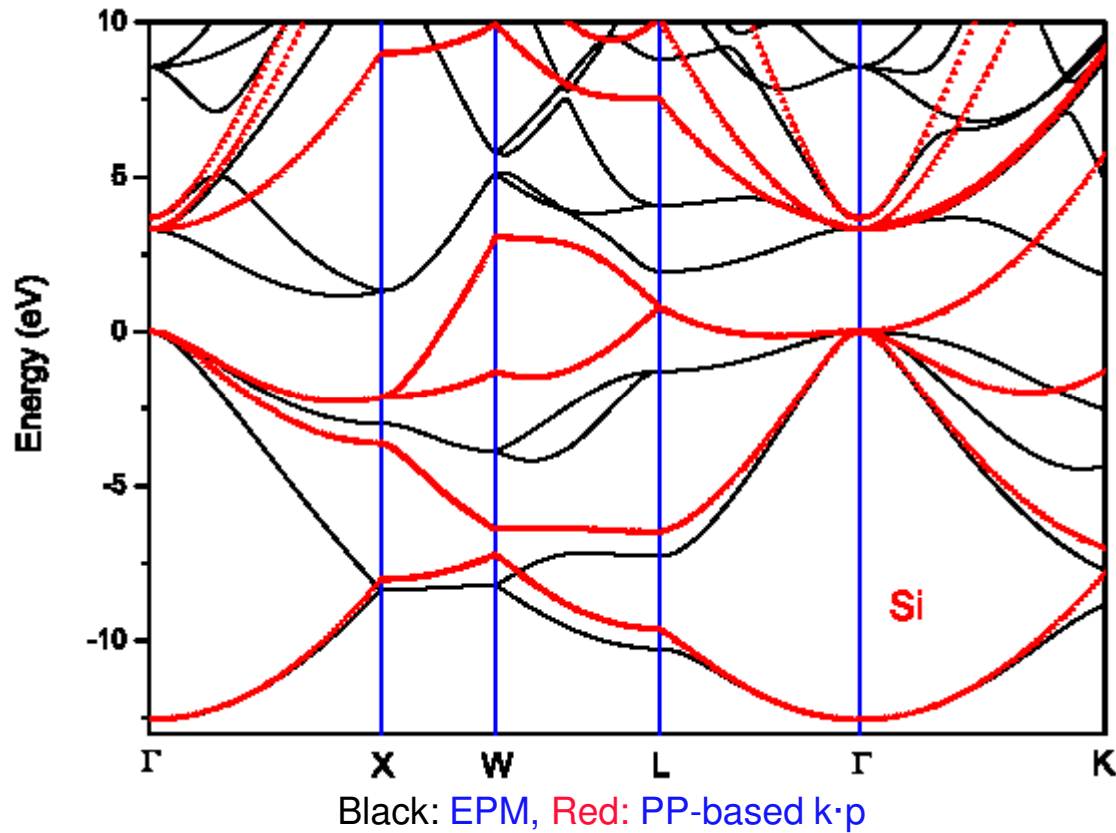
Demonstration on indirect bandgap se/c's: Si, Ge, SiC, Diamond

Si: 4-band k·p
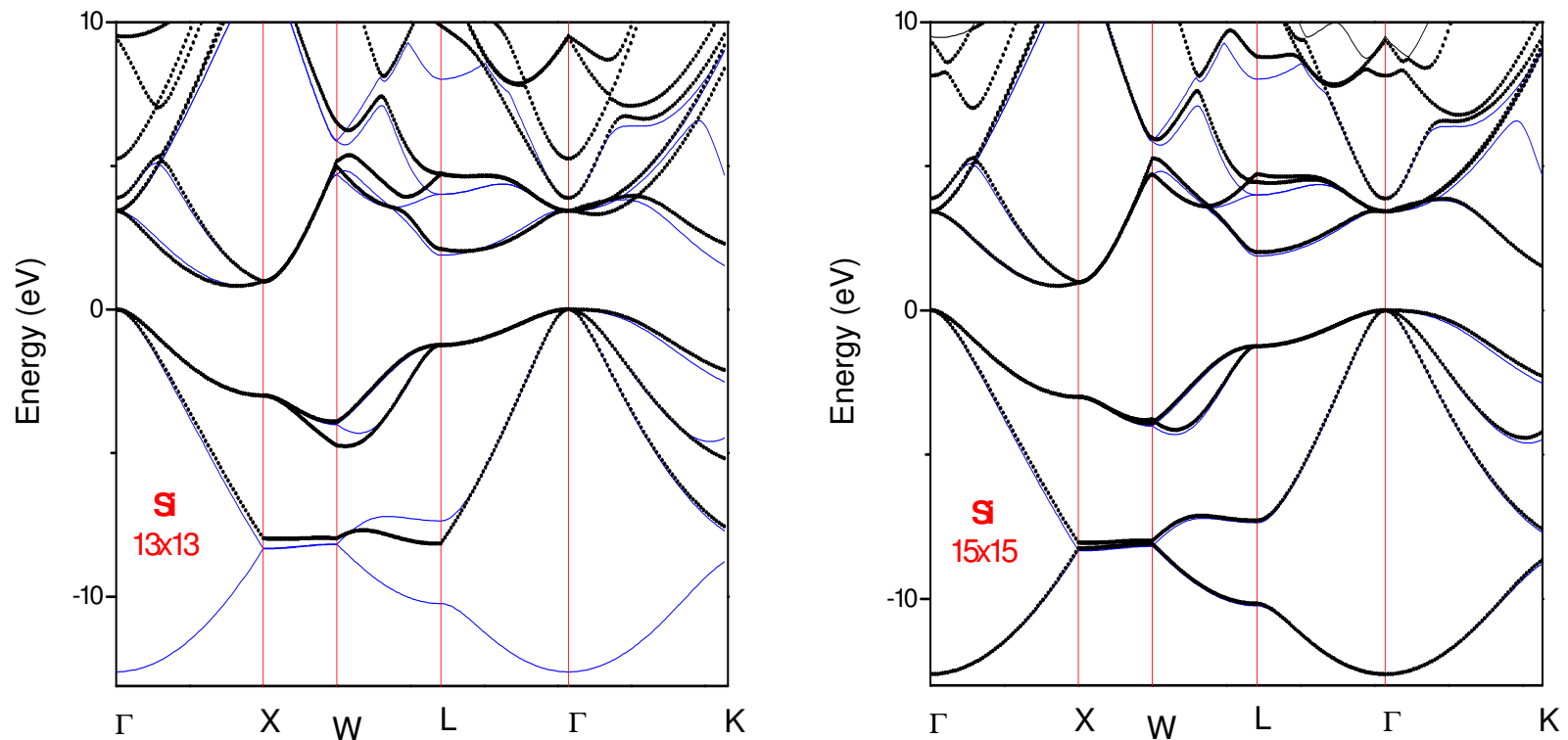

Black: EPM, Red: PP-based k·p

The selected expansion states are: from the Γ point we include the band indices 2 to 4 (with index 4 corresponding to valence band maximum), from the X point band 5 making altogether 4 states.

Si: 8-band k·p

Black: EPM, Red: PP-based k·p

The selected expansion states are all from the Γ point from bands 1 to 8.

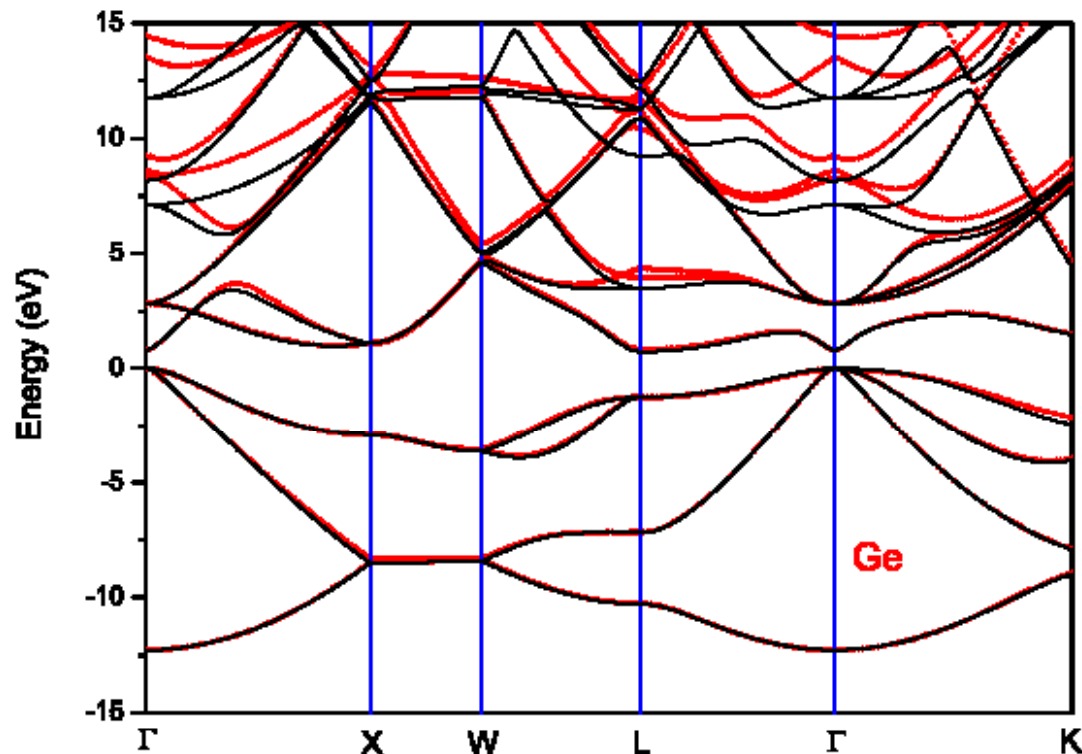# Si: Full-Zone with 13 and 15 band k·p

Blue: EPM, Black symbols: PP-based k·p

The selected expansion states are: from the Γ point we include the band indices 2 to 8 (with index 4 corresponding to valence band maximum), from the X point bands 3 to 6, and from the L point bands 3 and 4, making altogether 13 states. In the figure on the right we append the first Γ state and the fifth K states to further improve the overall bandstructure.
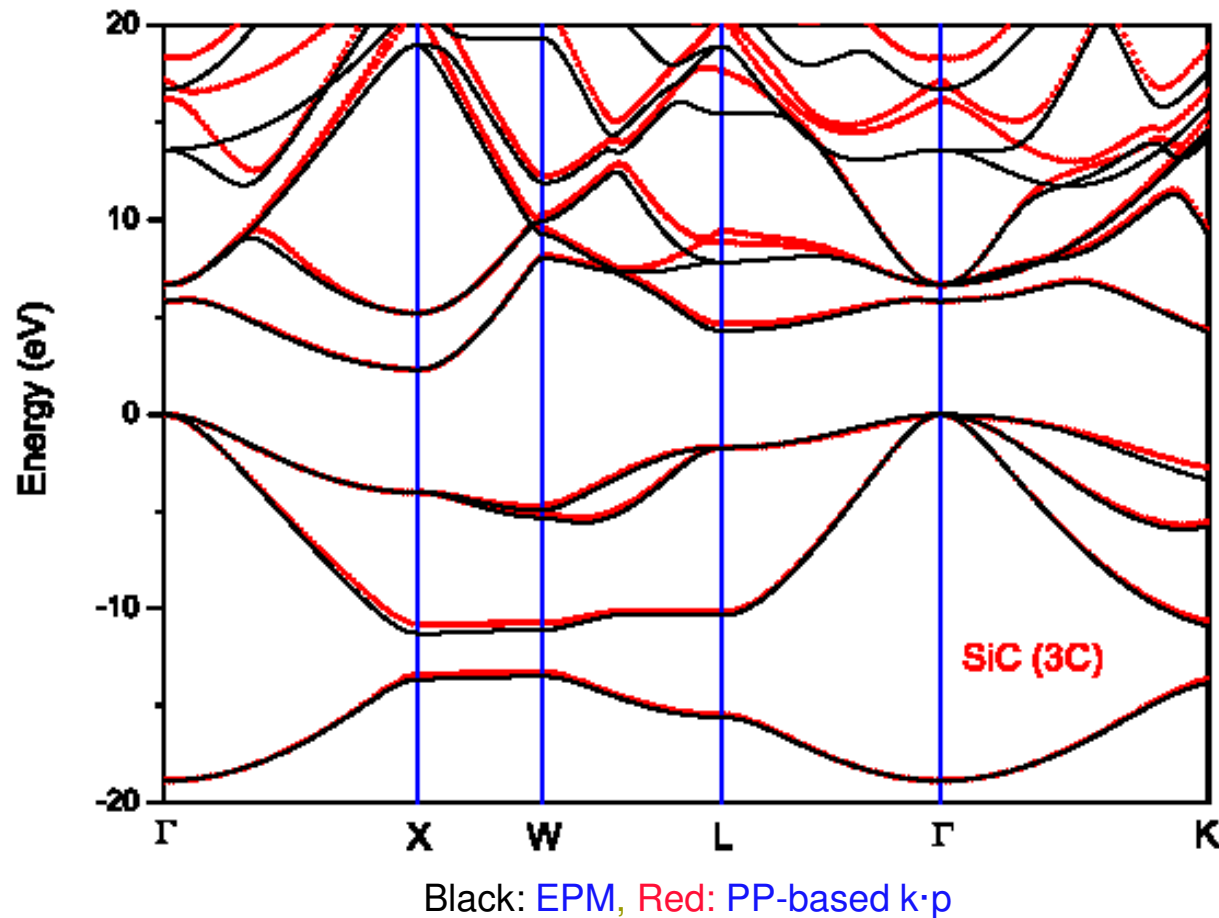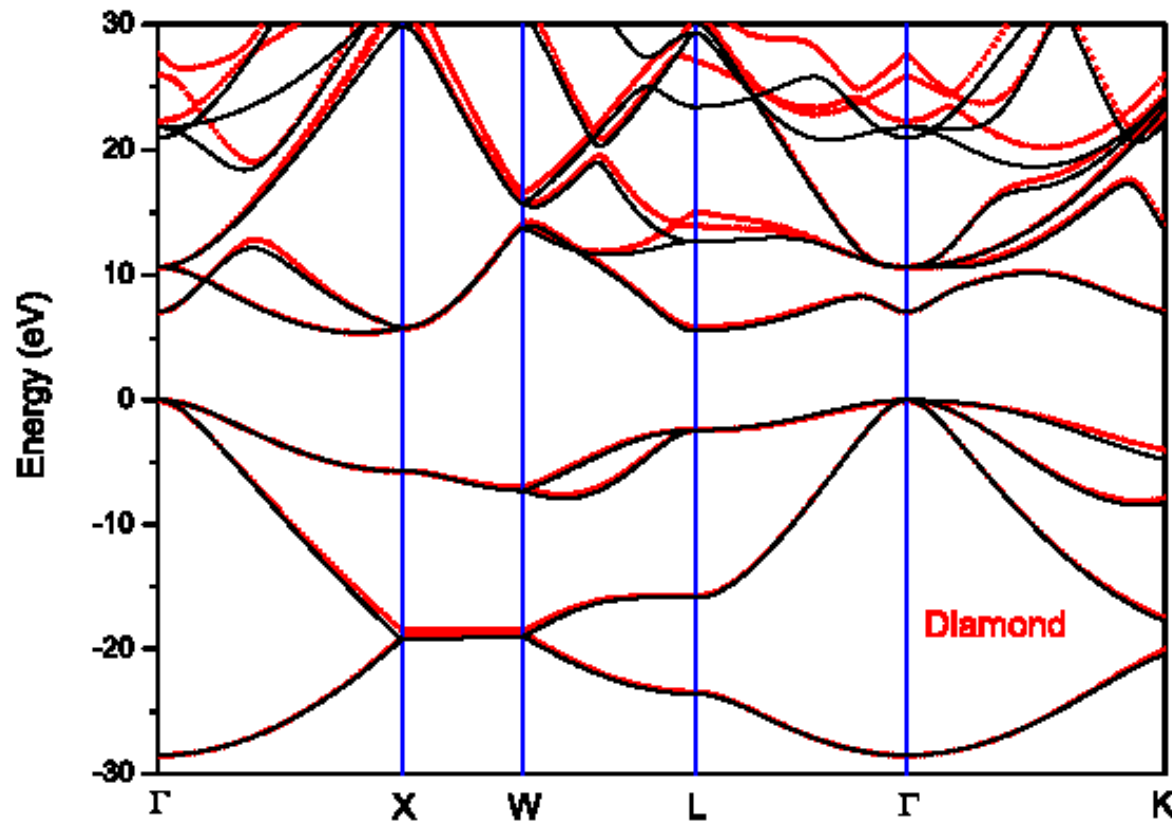
Ge: 15-band k·p

Black: EPM, Red: PP-based k·p

The selected expansion states are: from the Γ point we include the band indices 2 to 8 (with index 4 corresponding to valence band maximum), from the X point bands 3 to 6, and from the L point bands 3 and 4, first Γ state and the fifth K states making altogether 15 states.

SiC (Cubic Phase: 3C) 15-band k·p

Black: EPM, Red: PP-based k·p

[Same expansion basis set as before]

Diamond: 15-band k·p

Black: EPM, Red: PP-based k·p

[Same expansion basis set as before]

Agreement over 40 eV range