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Reciprocal space description of electrons and phonon states

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Overview of lecture

- Bloch’s Theorem
- Band Structure
- Density of States
- Examples
- Phonons

- NB Colour slides are available on the website

Bloch’s Theorem

Recap

- Bloch’s theorem: the density has the same periodicity as the potential, BUT the possible wavefunctions are all ‘quasi-periodic’:

$$\psi_k(\mathbf{r}) \;=\; e^{i\mathbf{k}.\mathbf{r}} u_k(\mathbf{r})$$

- We write $u_k(\mathbf{r})$ in a plane-wave basis as:

$$u_k(\mathbf{r}) \;=\; \sum_G c_{Gk} e^{i\mathbf{G}.\mathbf{r}}$$

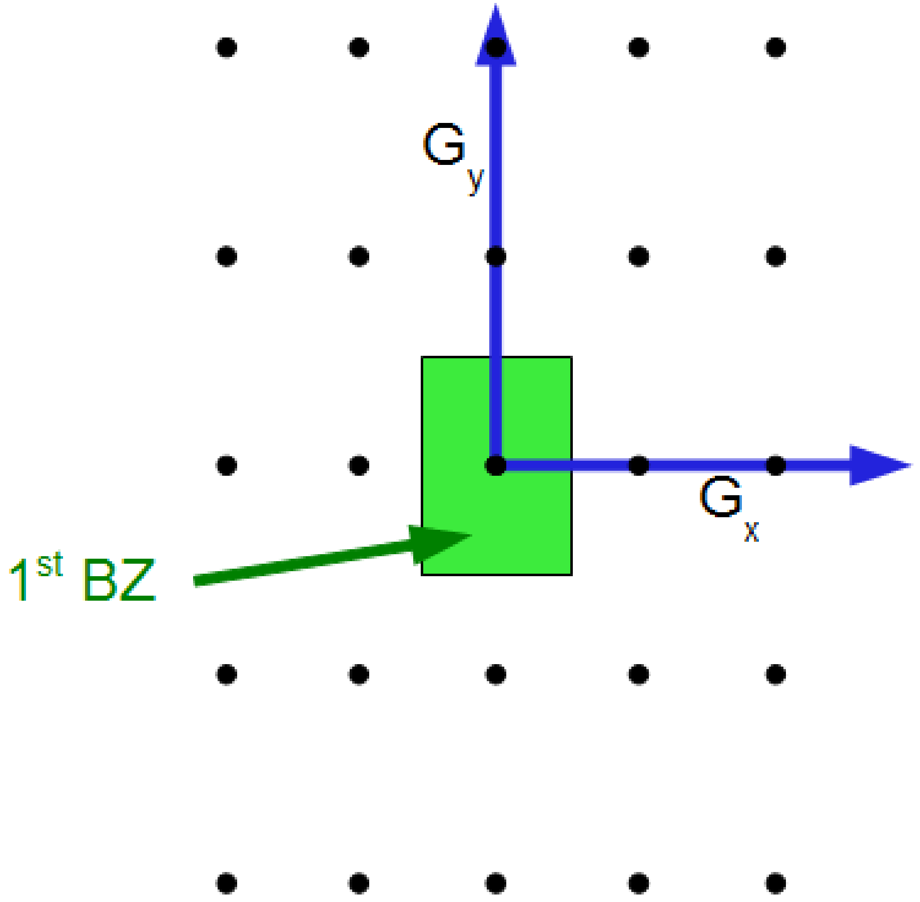
- where **G** are the reciprocal lattice vectors, defined so that $\mathbf{G}.\mathbf{L} = 2\pi m$.

1st Brillouin Zone

- Adding or subtracting **G** from **k** leaves properties unchanged
  - system is periodic in reciprocal-space too.
- Hence only need to study behaviour in the reciprocal-space unit cell
  - And then know how it behaves everywhere.
- Conventional to center unit cell around **G** = 0 (*a.k.a.* the Gamma point)
  - Call this the 1st Brillouin Zone.

2D Example

- The region of reciprocal space nearer to the origin than any other allowed wavevector is called the 1st Brillouin zone:.



Band Structure

E vs **k**

- How does the energy of states vary across the Brillouin zone?
- Consider one particular wavefunction:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}}u(\mathbf{r})$$

- Consider two different limits:
  - electrons with high potential energy,
  - and electrons with high kinetic energy.

Very localized electrons

- If an electron is trapped in a very strong potential, then we can neglect the KE:

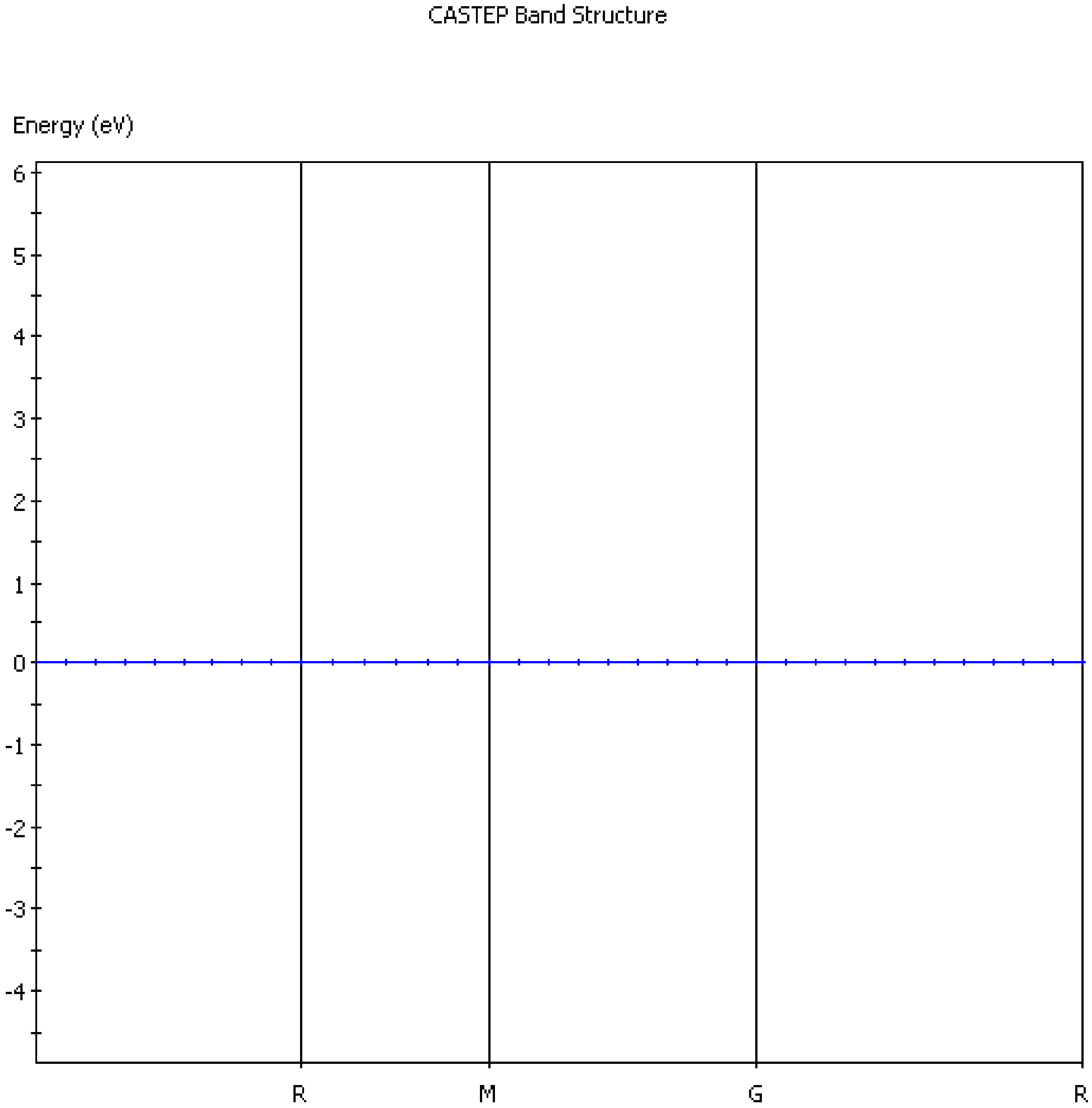
$$\hat{H} = \hat{V}$$

- The energy of our wavefunction is then

$$\begin{aligned} E(k) &= \int \psi^\star(\mathbf{r}) V(\mathbf{r}) \psi(\mathbf{r}) d^3\mathbf{r} \\ &= \int V(\mathbf{r}) |\psi(\mathbf{r})|^2 d^3\mathbf{r} \\ &= \int V(\mathbf{r}) |u(\mathbf{r})|^2 d^3\mathbf{r} \end{aligned}$$

- i.e. independent of **k**! So can just use **k** = 0.

H band structure (isolated)



Free electron limit

- For an electron moving freely in space then PE=0 and the Hamiltonian is just KE:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

- The eigenstates of the Hamiltonian are just plane-waves – i.e. c_{Gk} = 0 except for one particular **G**.
- Our wavefunction is now

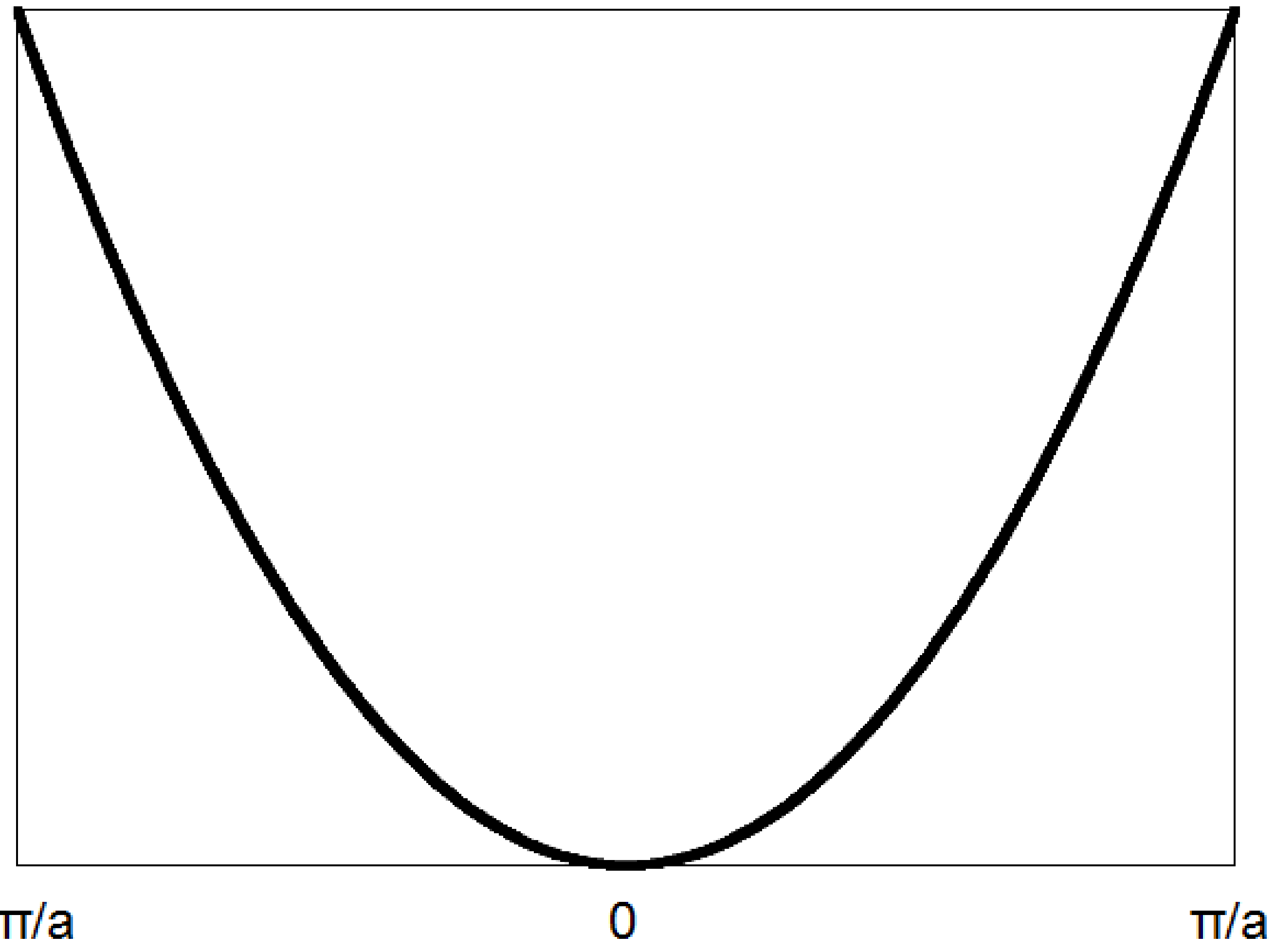
$$\begin{aligned} \psi(\mathbf{r}) &= c_G e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}} \\ \Rightarrow \nabla^2\psi(\mathbf{r}) &= -(\mathbf{k}+\mathbf{G})^2\psi(\mathbf{r}) \end{aligned}$$

Free electrons

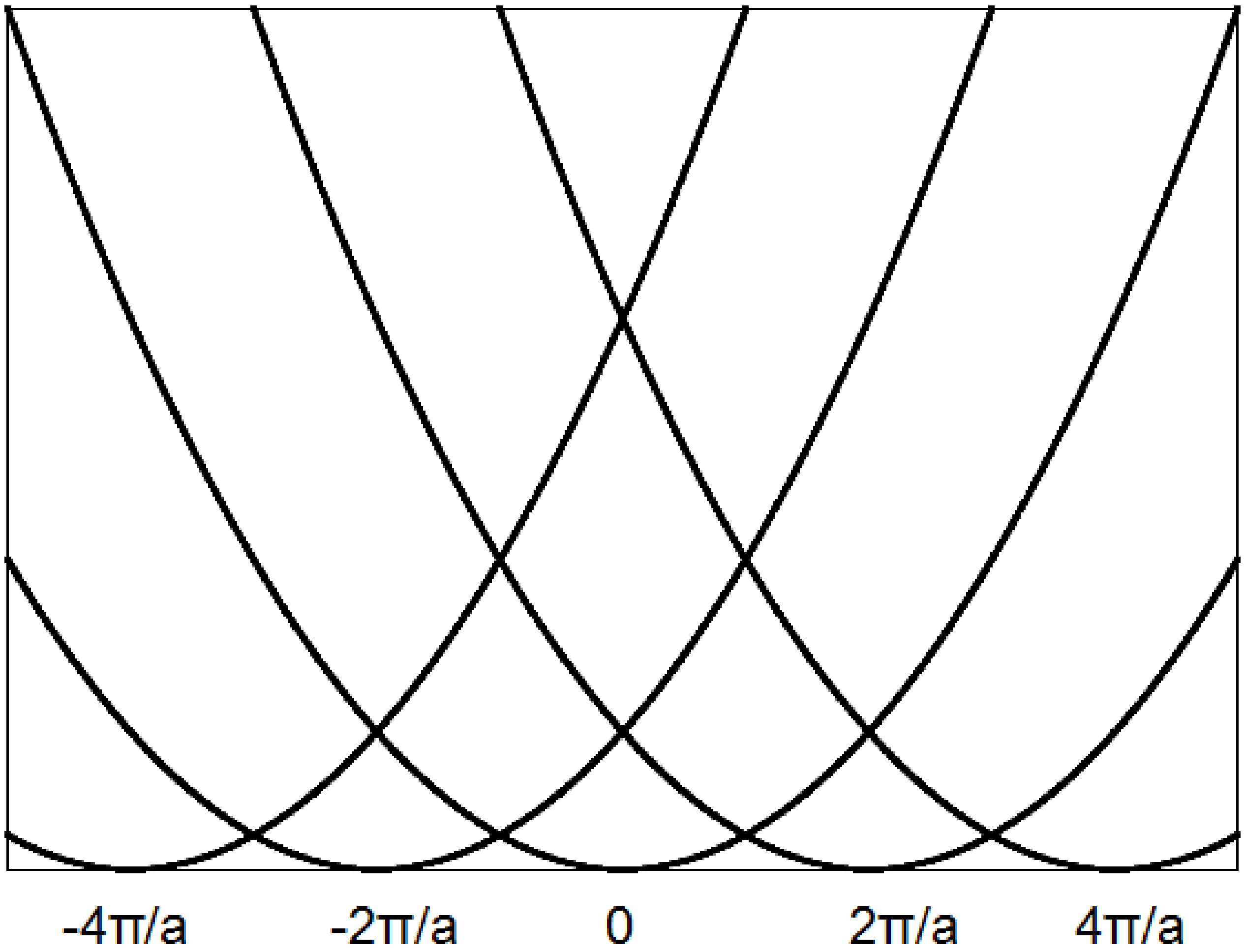
$$\begin{aligned} E(\mathbf{k}) &= -\frac{\hbar^2}{2m}\int \psi^\star(\mathbf{r})\nabla^2\psi(\mathbf{r})d^3\mathbf{r} \\ &= \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2\int \psi^\star(\mathbf{r})\psi(\mathbf{r})d^3\mathbf{r} \\ &= \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2 \end{aligned}$$

- So $E(\mathbf{k})$ is quadratic in **k**, with the lowest energy state at **G** = 0
- Each state has energy that changes with k => forms an *energy band* in reciprocal space

Free electron bands

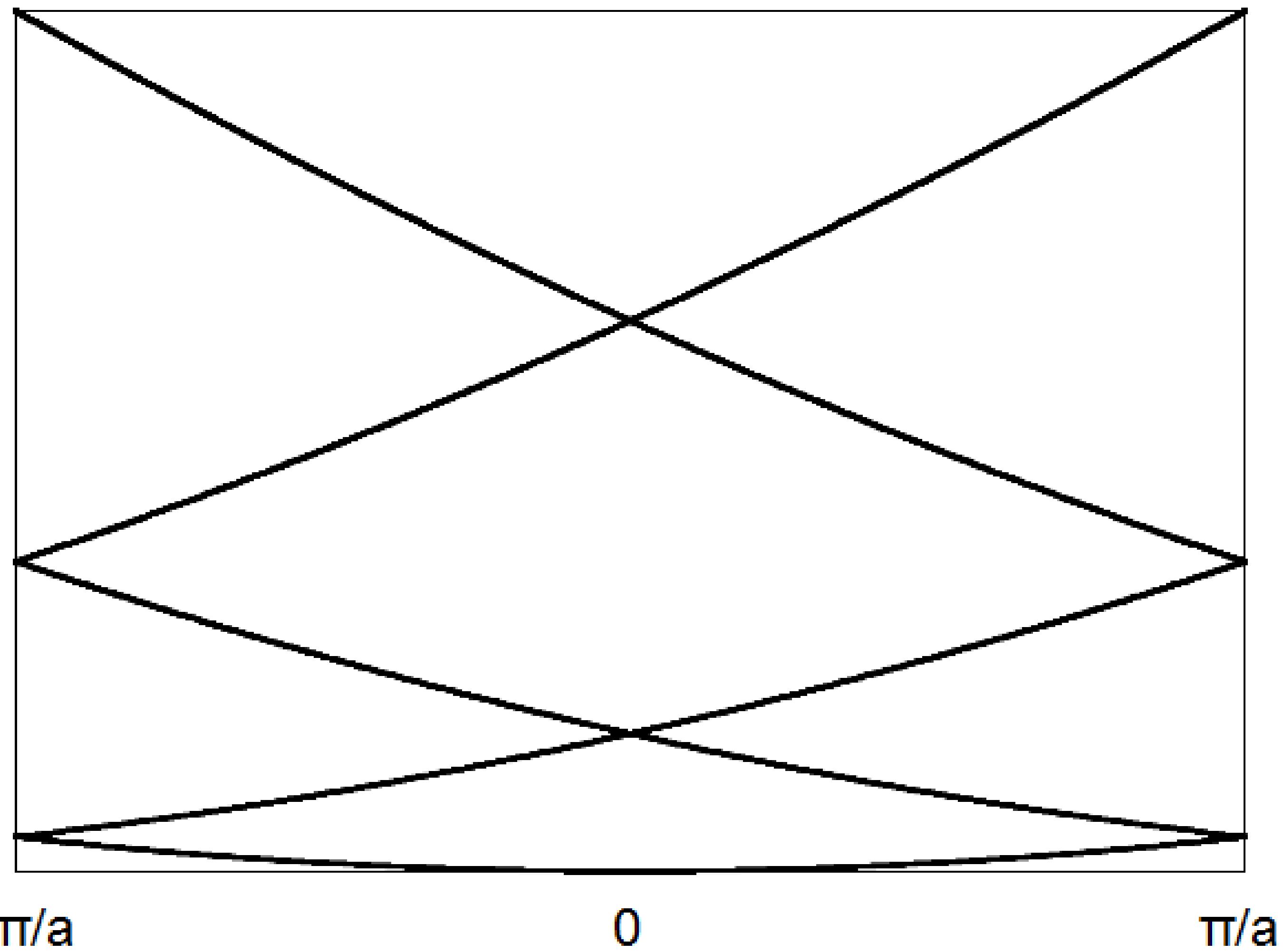


Free electron bands



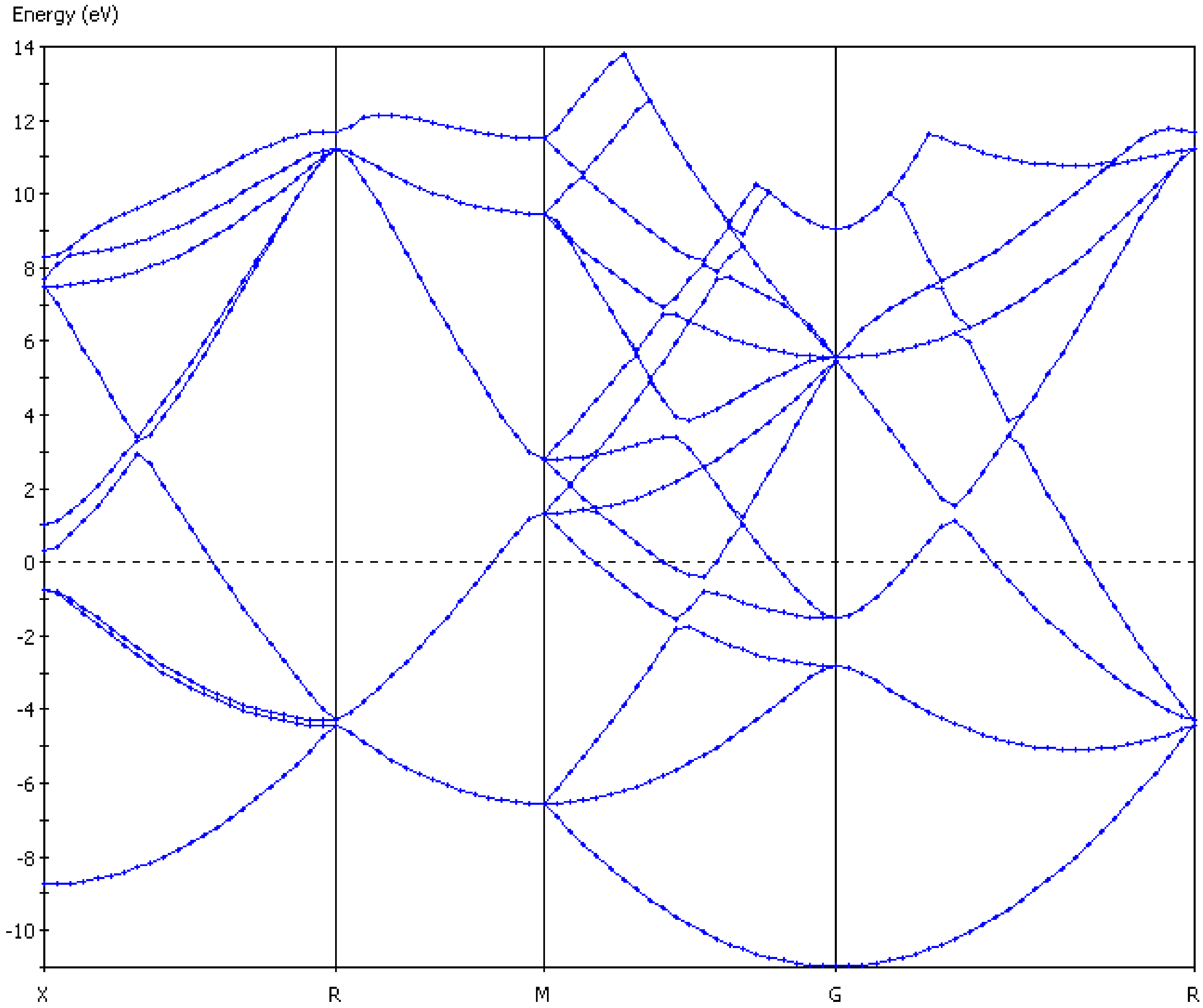
- But states are periodic in reciprocal space => get parabola about each lattice point

Free electron bands



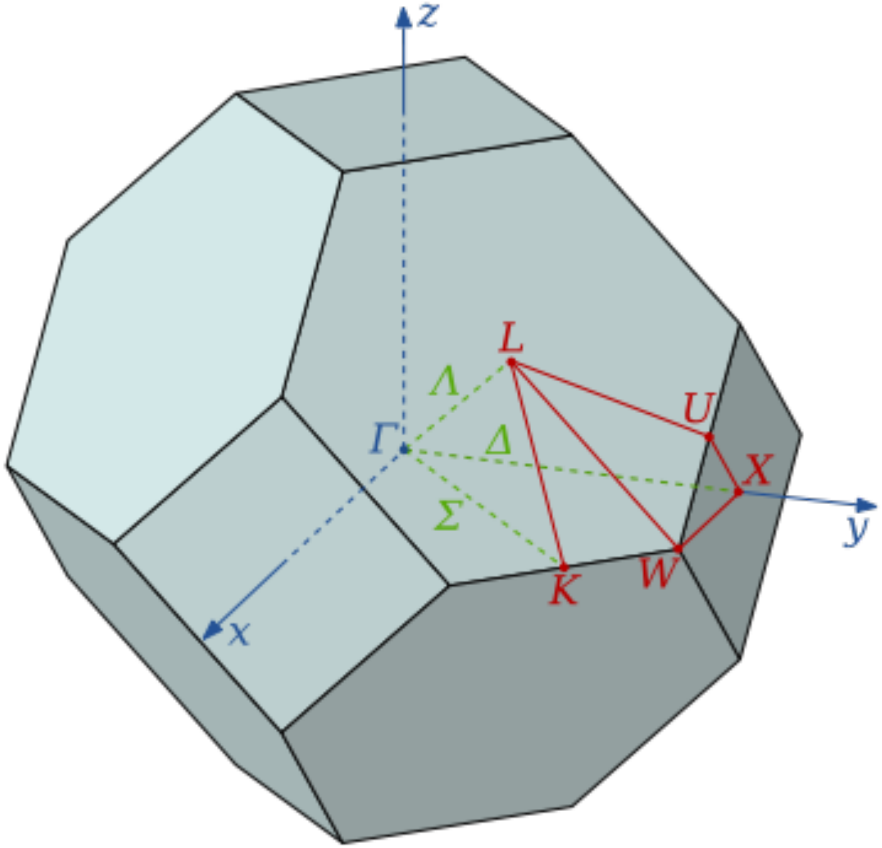
- But states are periodic in reciprocal space => fold back using **G**'=**G**$\pm$m.2π/**L**

Al - a nearly free electron metal



3D Brillouin Zone

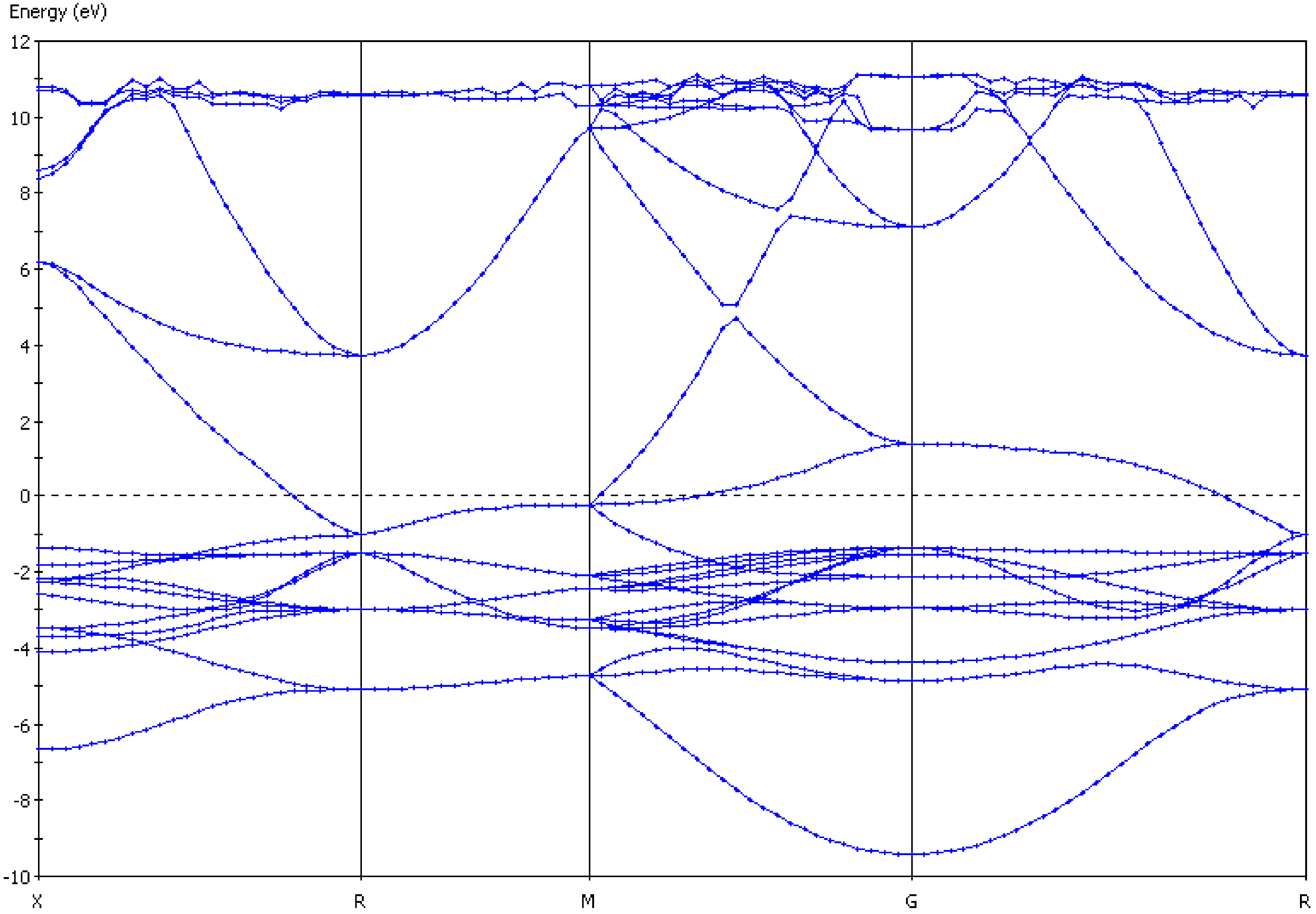
- More complex in 3D
- The reciprocal lattice vectors are not simple cubic and the BZ can vary a lot:



Band structure

- The way the energies of all of the states change with **k** is called the *band structure*.
    - **k** is a 3D vector so E(**k**) is hard to visualize
- Conventional to plot energies along special high-symmetry directions.
    - These energies represent either max or min energies for the bands across the whole BZ.
- In real materials electrons are neither completely localised nor completely free
    - But still see these features in band structures.

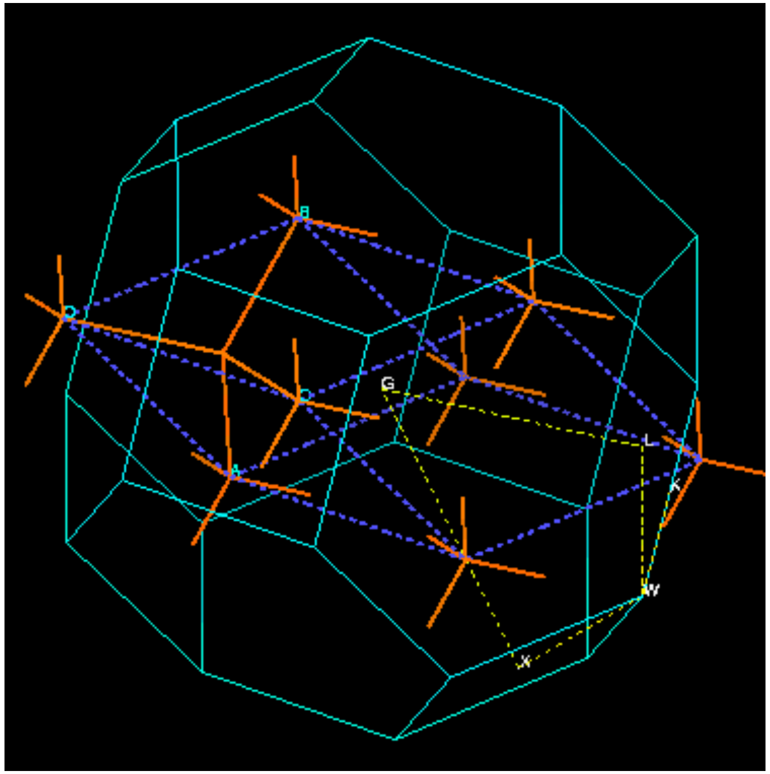
Band structure of Cu

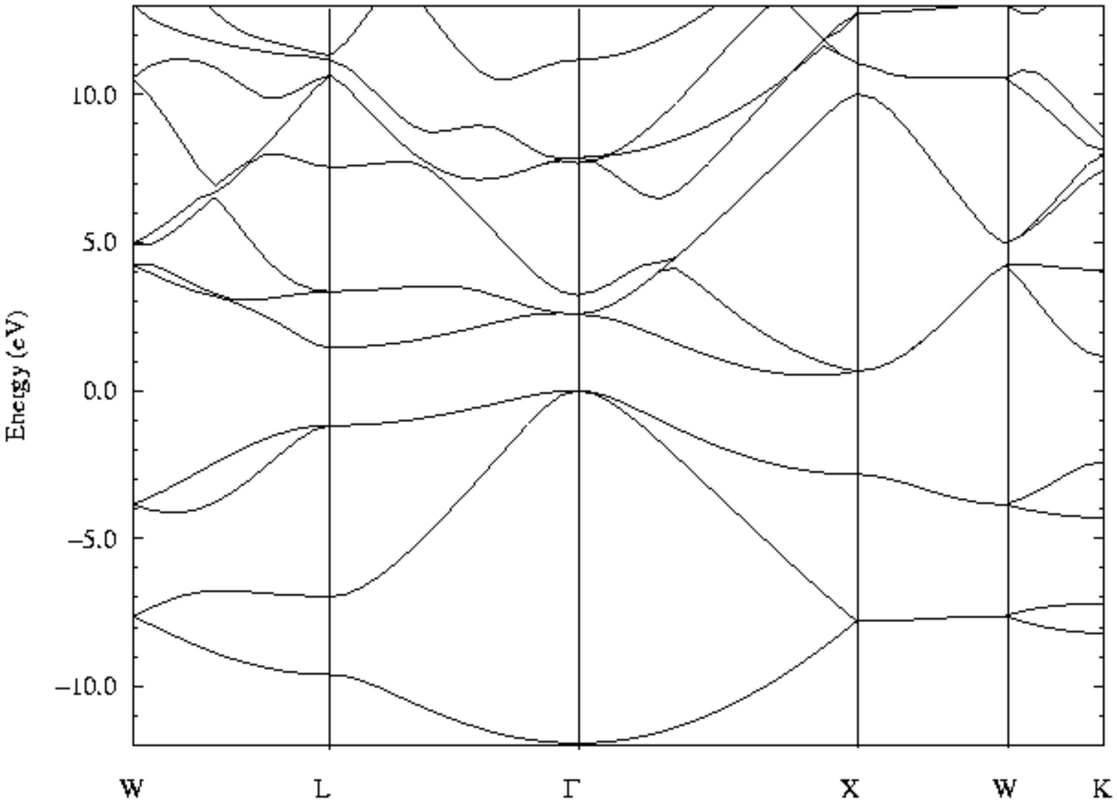


Electronic transitions

- Electrons are Fermions and obey Pauli exclusion principle
  - Lowest N_e states are occupied by electrons
  - At T=0 K all states below the *Fermi energy*, E_F , are occupied and states above are empty
  - Band-structures often shifted so $E_F = 0$
- In semi-conductors and insulators there is a region of energy just above E_F with no bands – the *band gap*.

Band structure of Si





Density of States

Density of States

- The band structure is a good way to visualise the *dispersion* (wavevector-dependence) of the energy states
  - Ditto the band-gap, the possible electronic transitions, etc.
- But the transition probability depends on how many states are available in the initial and final energies (e.g. Fermi golden rule).
  - Band structure only tells you about the bands along high symmetry directions.

DOS

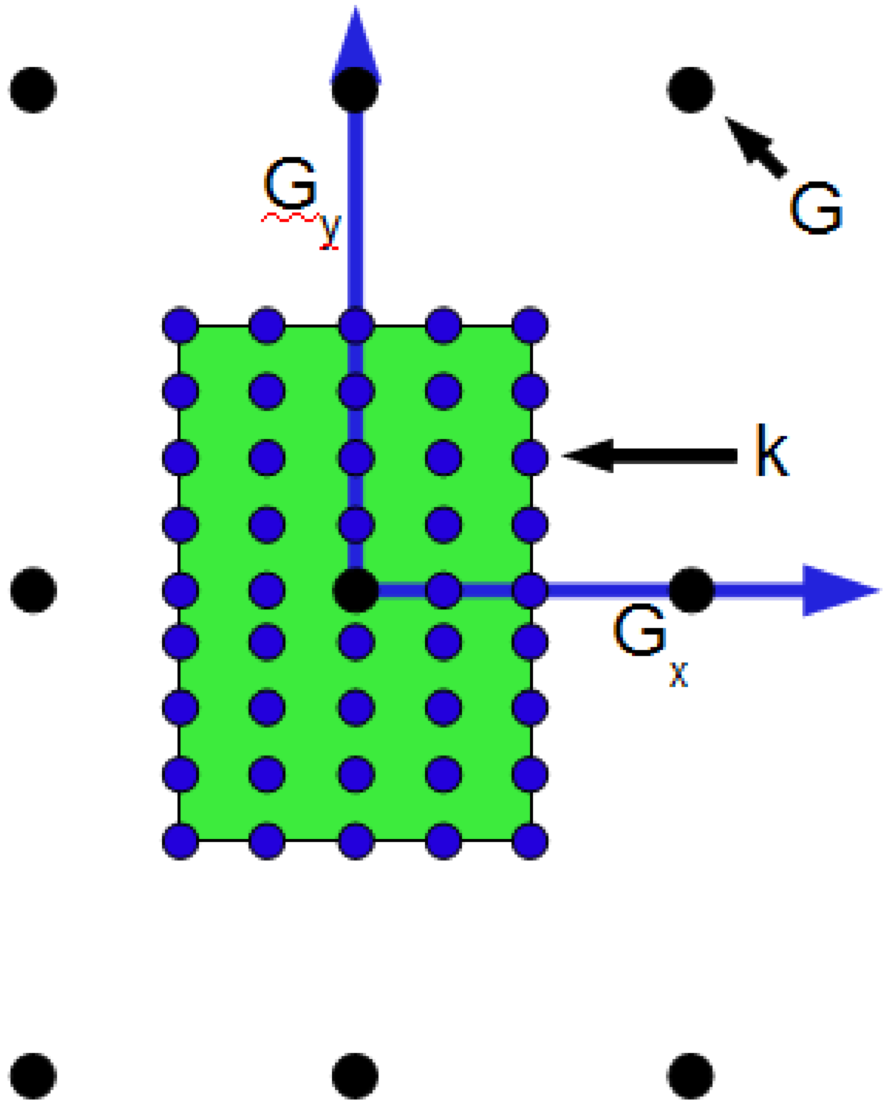
- What we need is the full density of states (DOS) across the whole BZ
  - Not just the special directions.
- The density of states is $g(E) = \frac{1}{\Omega_G}\frac{dN}{dE}$

where Ω_G is the volume of reciprocal space associated with each **G**-vector.

- We have to uniformly sample the BZ, just as for the calculation of the ground state electronic structure.

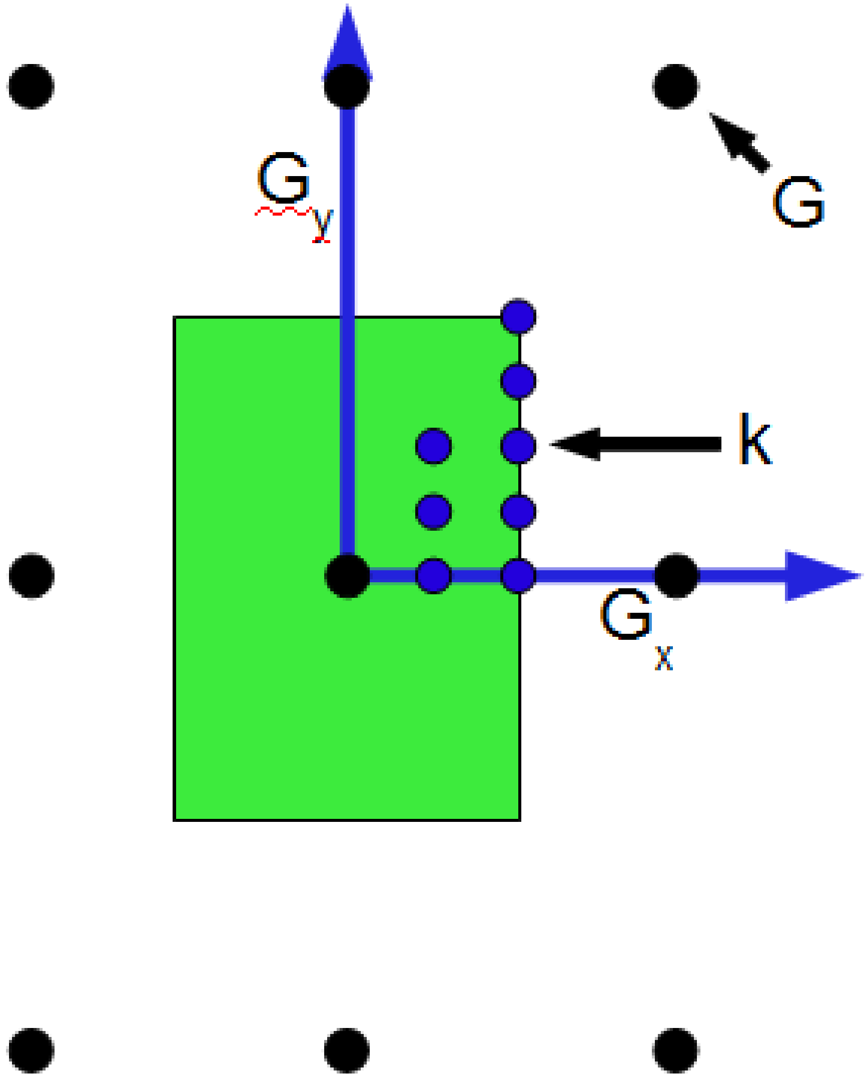
Sampling DOS

- Full DOS



Sampling DOS

- Equivalent DOS using crystal symmetry to reduce sampling region to the *irreducible wedge*

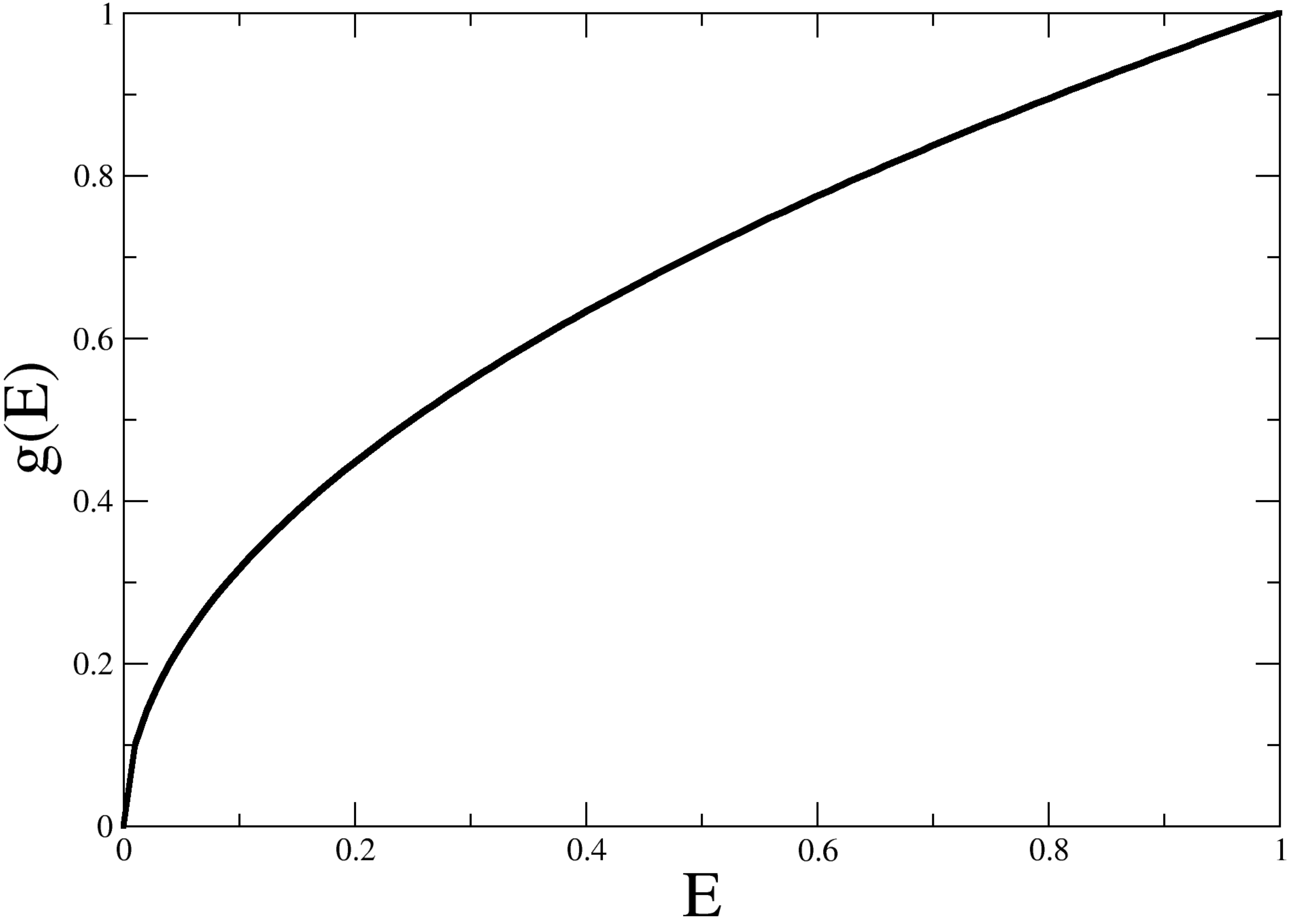


DOS for Free Electrons

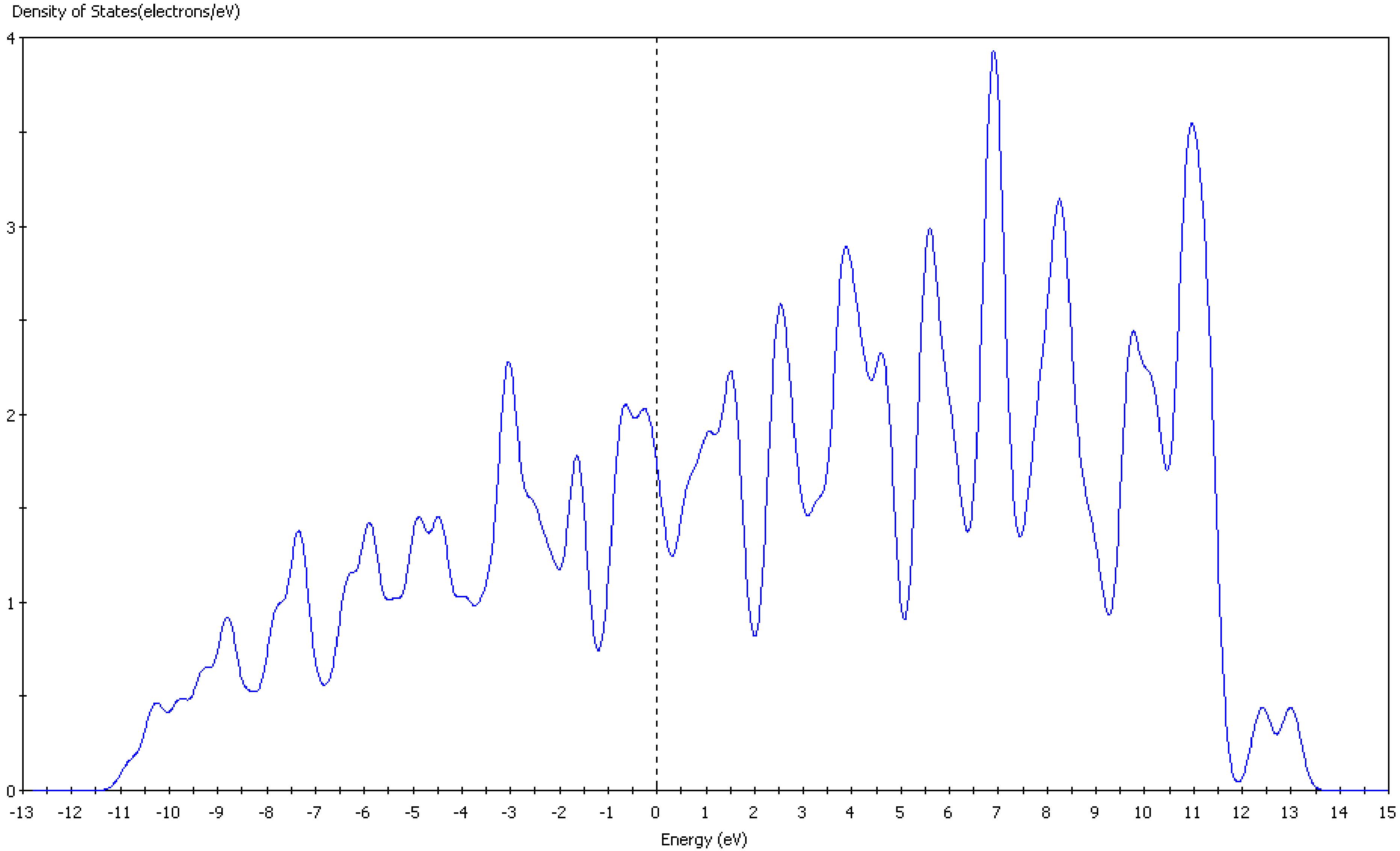
- For free electrons we saw $E(\mathbf{k}) \propto (\mathbf{k}+\mathbf{G})^2$
- So for a fixed *E* the **k**-vectors form a spherical shell of area $4\pi|\mathbf{k} + \mathbf{G}|^2$

$$
\begin{aligned}
\frac{dN}{dk} &\propto |\mathbf{k}+\mathbf{G}|^2 \\
\Rightarrow g(E) &= \frac{1}{\Omega_G}\frac{dN}{dE} = \frac{1}{\Omega_G}\frac{dN}{dk}\frac{dk}{dE} \\
&\propto |\mathbf{k}+\mathbf{G}|^2 \frac{1}{|\mathbf{k}+\mathbf{G}|} \\
&\propto \sqrt{E}
\end{aligned}
$$

Ideal DOS



DOS of Al


Density of States(electrons/eV)
4
3
2
1
0
-13
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Energy (eV)

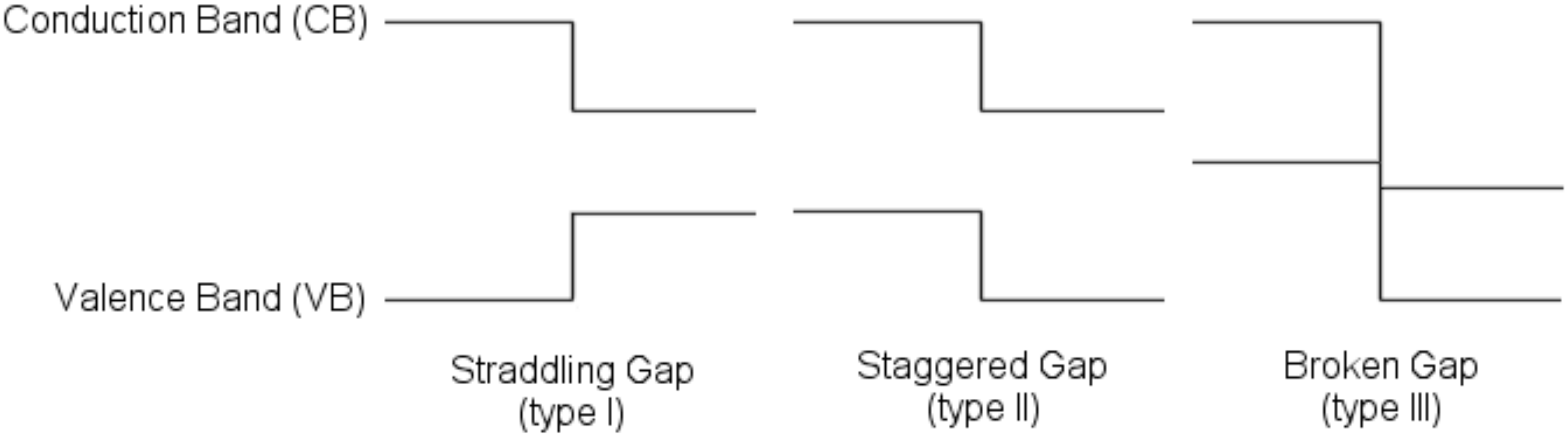
Computing a DOS

- Computing a band structure or a DOS is straightforward:
  - First compute the ground state electronic density with a good **k**-point sampling
  - Then fix the density, and find the states at the band structure/DOS **k**-points
  - The difference between DOS and band structure is only in the choice of sample **k**
- NB As the density is fixed for the second calculation, it takes much less time per **k**-point than the original ground state calculation.

Example –
Band Offsets

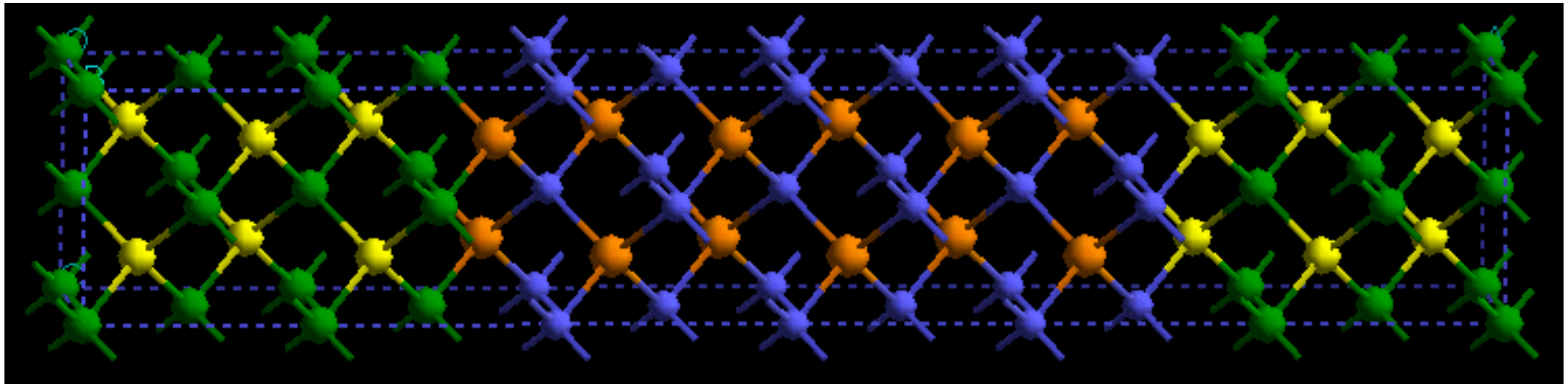
Application – Band Offsets

- Heterojunctions are formed when two different types of semiconductor are joined together.
- Heterostructures are used extensively in the electronic (e.g. transistors) and optoelectronic (e.g. LED’s) industry.



Calculating Band Offsets

- Knowledge of the band structures of the two individual materials is not sufficient to determine the band offset.
- Band energies are determined with respect to the average potential in the solid.
- It is also necessary to perform a *supercell* calculation to determine how the potentials are lined up with respect to each other.



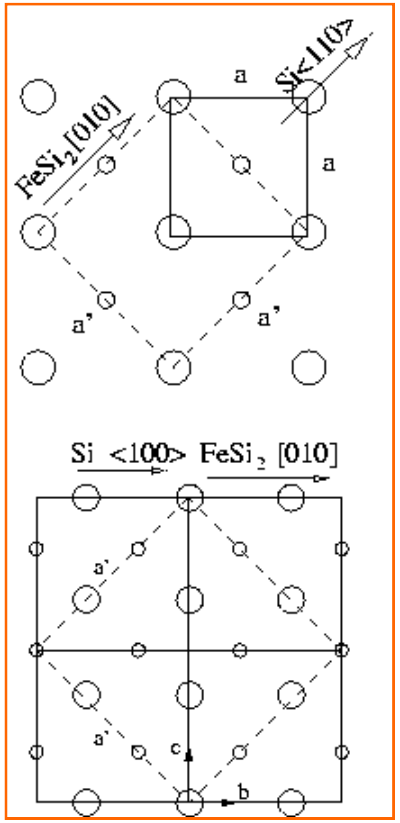
The Average Potential

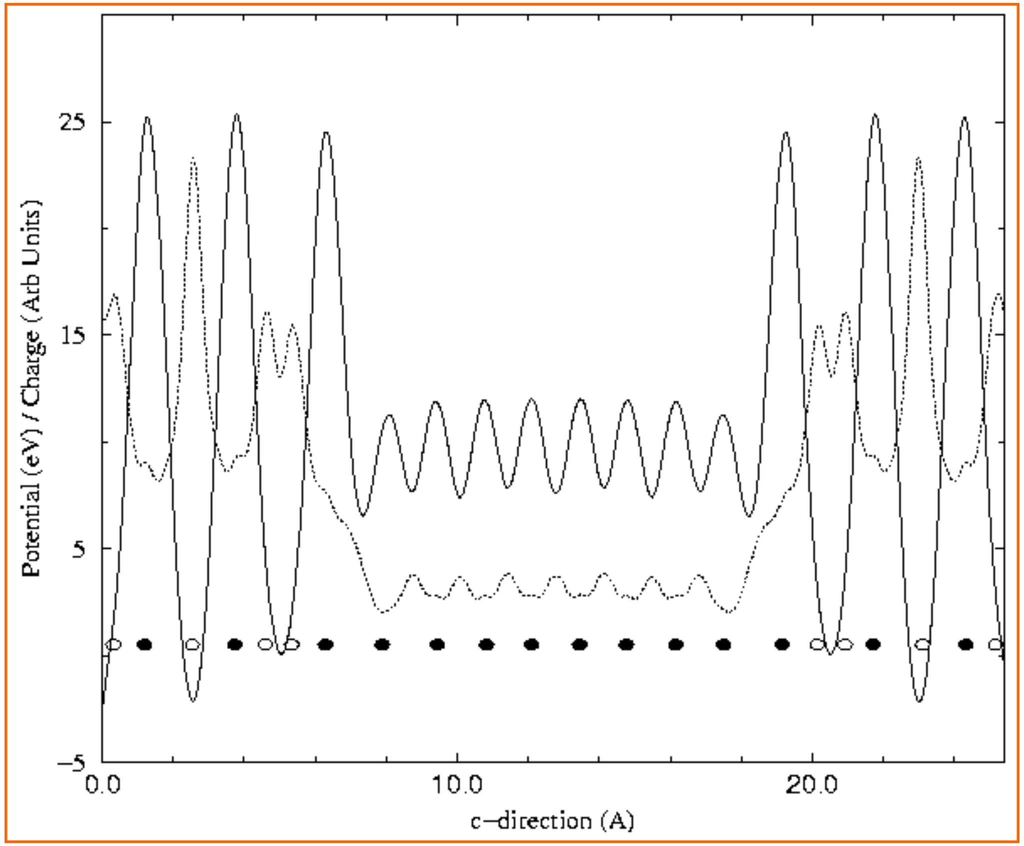
- The potential can be averaged across the *x-y* planes (junction normal to *z*).
- This is the *microscopic average* potential.
- The *macroscopic average* potential is calculated over the period over the microscopic potential.
- The band structures are measured relative to the macroscopic average.

$$\overline{\overline{V}}_{tot}(z) = \frac{1}{\lambda\lambda'}\int_{z-\lambda/2}^{z+\lambda/2}\int_{z'-\lambda'/2}^{z'+\lambda'/2}\overline{V}_{tot}(z'')dz''dz'$$

- Can then use this to do *band line-up*

An Example: FeSi$_2$ on Si



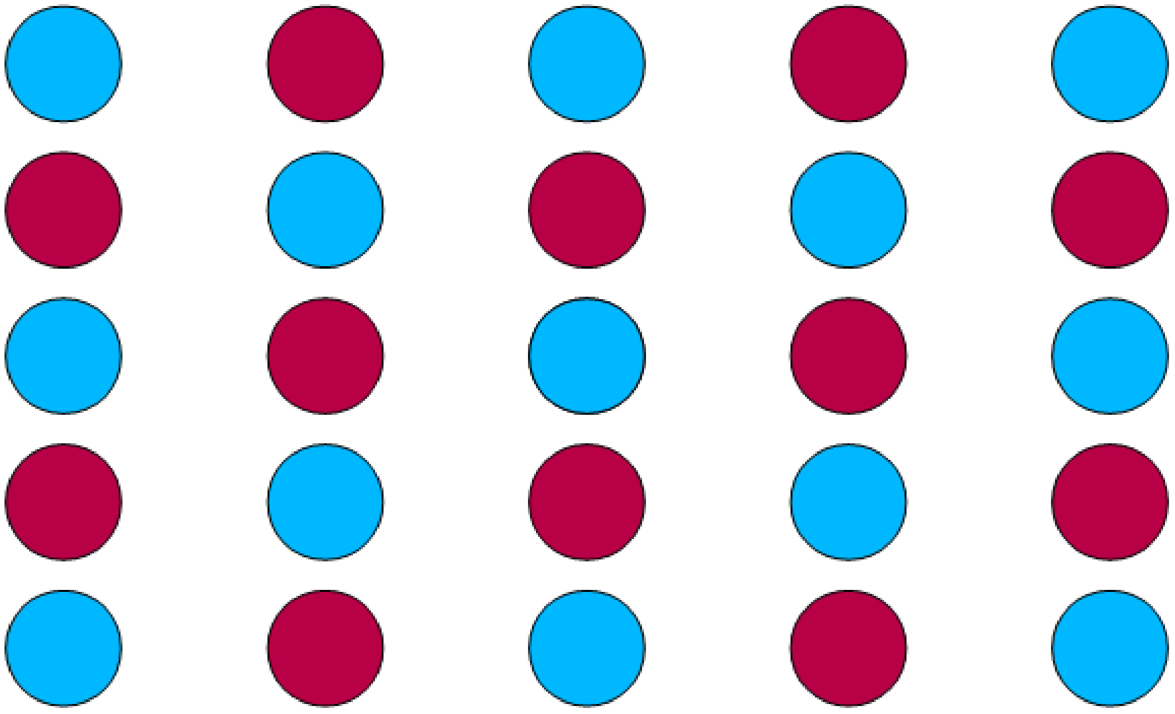


Offset is 0.4eV – useful for LED’s and near-IR detectors

Phonons

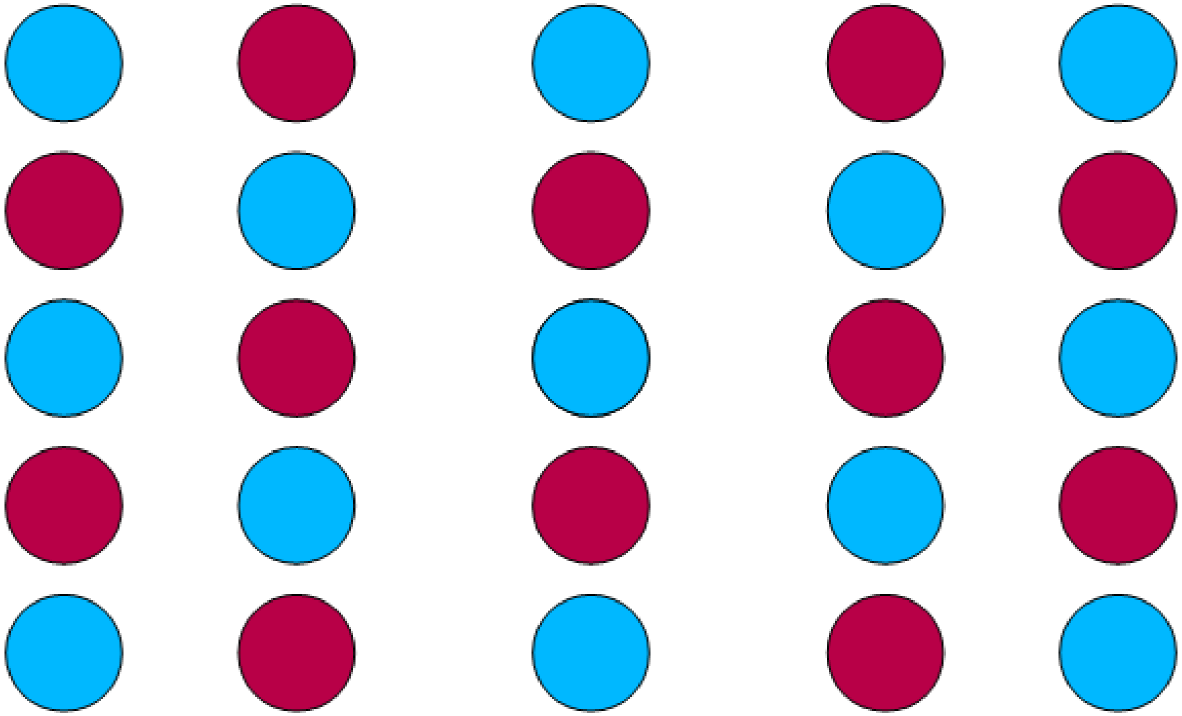
Phonons

- A crystal is more than just electrons – contains ions/atoms and quasi particles such as phonons etc.



Phonons

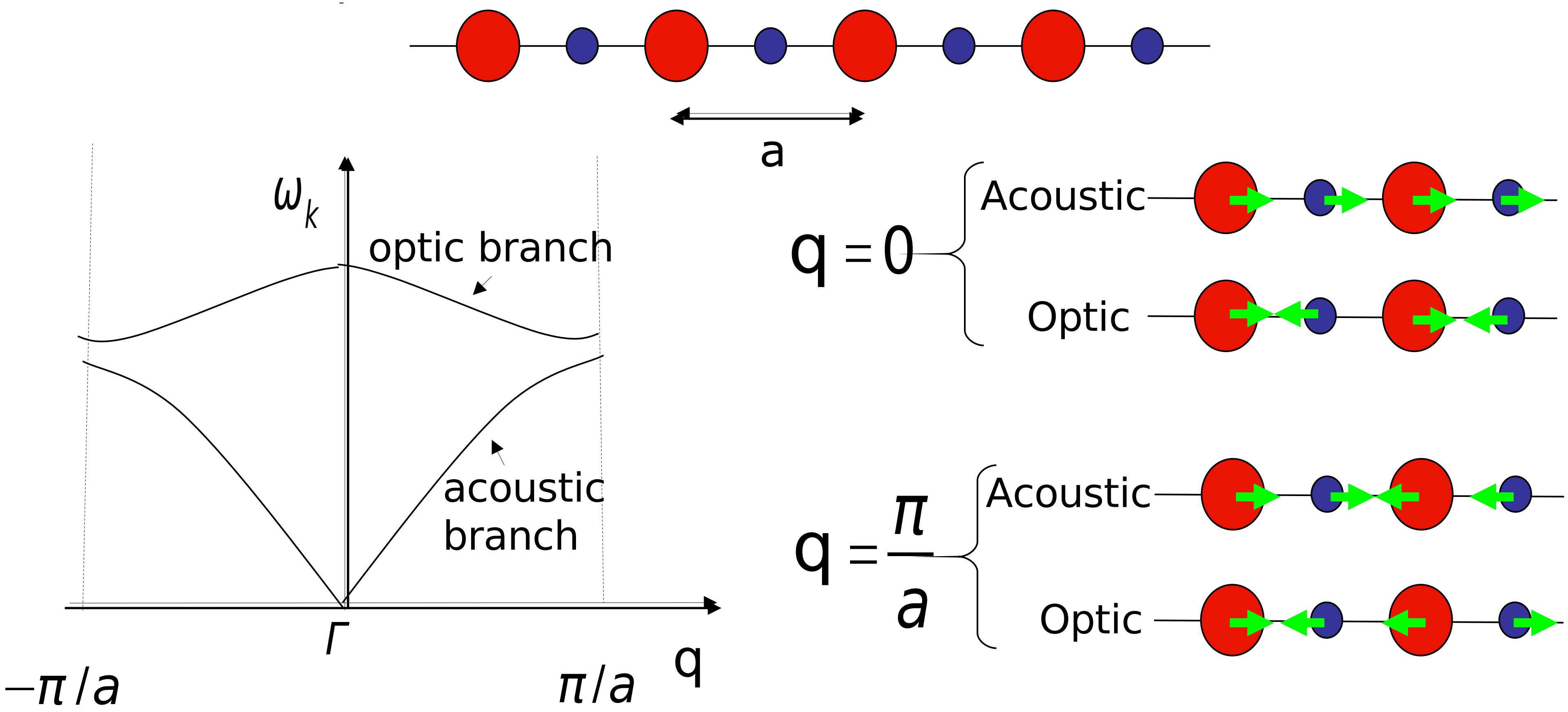
- What is a phonon? A quantized lattice vibration of a crystal
- When a sound wave travels through a crystal, it creates a periodic distortion:



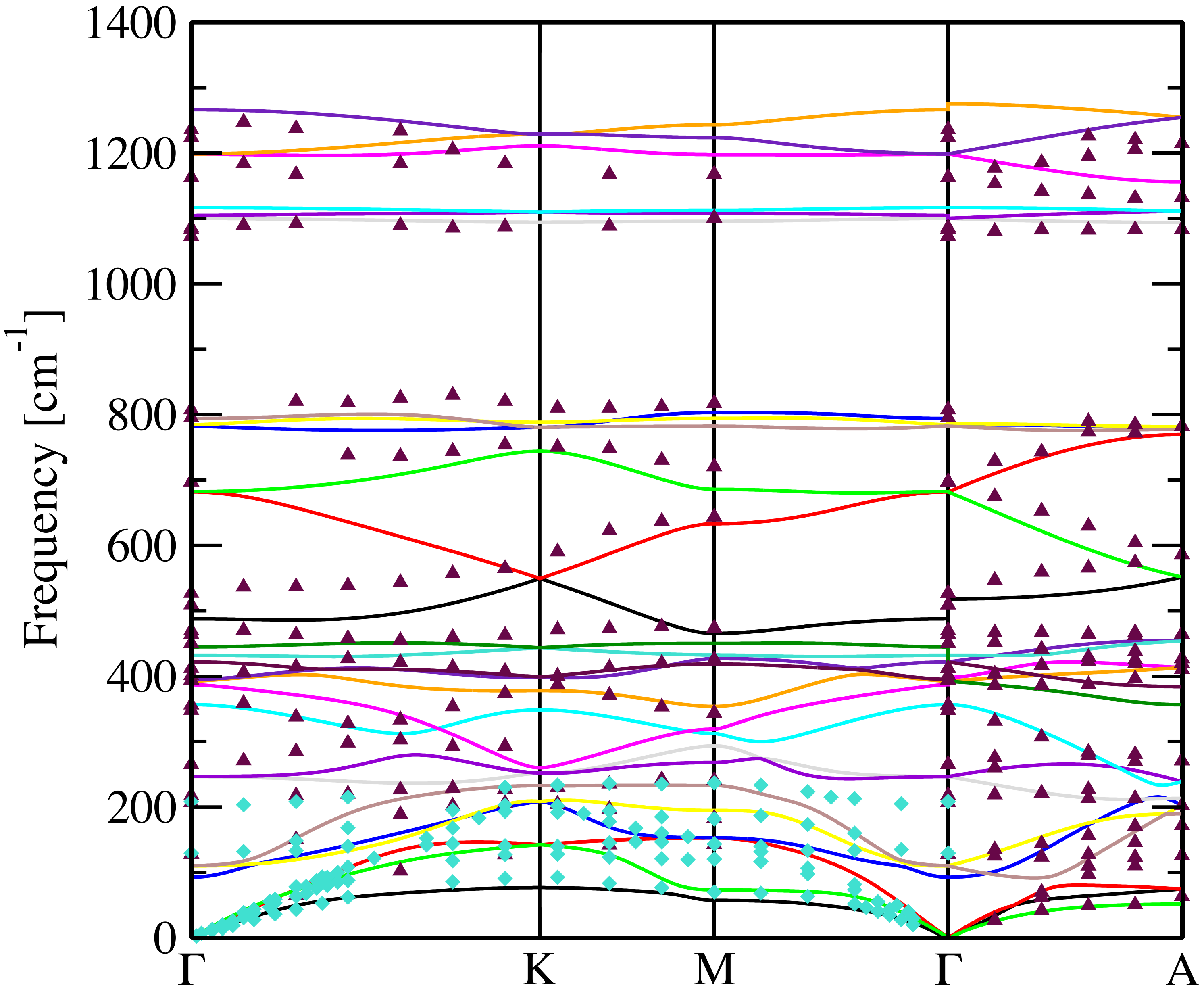
Phonon dispersion

- The periodic distortion means a wavevector **q**
  - Another reciprocal space quantity – do not confuse with **k** or **G**!
- Distortion is real so: $d_q(\mathbf{r}) = a_q \cos(\mathbf{q}.\mathbf{r})$
- Can plot a *phonon* band structure.
  - Usually plot frequency ω against **q**, not *E*.
  - Shows frequency of different lattice vibrations, from long-wavelength acoustic modes to the shorter optical ones
  - Negative ω means structural instability …

Phonon dispersion



α-quartz: CASTEP vs Expt



Summary

Summary

- Reciprocal space is very useful
  - Provides natural language for describing periodic systems
  - All the periodic responses are contained within the 1st Brillouin Zone
- Can calculate E(**k**) for the electrons
  - Band structure => special directions in BZ
  - Density of states => uniform sampling of BZ
- Exactly the same language and concepts apply to phonons – quantized lattice vibrations