

# Electron Bands in Crystals

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# Periodic Crystals

(The discussion here follows Ashcroft and Mermin, "Solid State Physics", Chapters 4-8.)

A crystal is an ordered state of matter in which the positions of the nuclei (and consequently all properties) are repeated periodically in space. A crystal is much simpler than a general disordered structure such as a liquid or amorphous material. It is specified by the positions of the nuclei in the smallest possible repeat unit (a primitive unit cell), and the rules that describe the repetition (translations).

- The positions and types of atoms in the unit cell is called the basis, and the set of translations generates the entire periodic crystal by repeating the basis. The set of translation vectors is a lattice of points in space called the Bravais lattice.

This can be summarized as:

**Crystal structure = Bravais lattice + basis.**

- The order is described by symmetry operations. The set of translations form a group of operations. The sum of any two translations is another translation, and the set of all translations forms the translation group. In addition there may be other operations that leave the crystal the same, such as rotations, reflections, and inversions.

This can be summarized as:

**Space group = translation group + point group.**

# Translation Symmetry in Crystals

Here we will deal only with translations which are intrinsic to all crystals. The possible translations form a lattice in space, which has dimension  $d$ . In some places the formulas will be for  $d=3$ , but they are easily generalized to any dimension. Any translation can be written as integral multiples of primitive vectors,

$$\mathbf{T}(n_1, n_2, \dots) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + \dots \quad (1)$$

where the vectors  $\mathbf{a}_i$ ,  $i = 1, d$  are the primitive translation vectors of the lattice.

Examples: (here  $a$  is the unit of length)

- line:  $\mathbf{a}_1 = a$ .
- square:  $\mathbf{a}_1 = (1, 0)a$ ;  $\mathbf{a}_2 = (0, 1)a$ .
- triangular:  $\mathbf{a}_1 = (1, 0)a$ ;  $\mathbf{a}_2 = (\frac{1}{2}, \frac{\sqrt{3}}{2})a$ .
- simple cubic:  $\mathbf{a}_1 = (1, 0, 0)a$ ;  $\mathbf{a}_2 = (0, 1, 0)a$ ;  $\mathbf{a}_3 = (0, 0, 1)a$ .
- face centered cubic  $\mathbf{a}_1 = (\frac{1}{2}, \frac{1}{2}, 0)a$ ;  $\mathbf{a}_2 = (\frac{1}{2}, 0, \frac{1}{2})a$ ;  $\mathbf{a}_3 = (0, \frac{1}{2}, \frac{1}{2})a$ .
- body centered cub.  $\mathbf{a}_1 = (\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})a$ ;  $\mathbf{a}_2 = (\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})a$ ;  $\mathbf{a}_3 = (-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})a$ .

In matrix notation these may be written (where each row is the cartesian components of a primitive translation vector):

$$sq : \mathbf{a} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} a; \quad tri : \mathbf{a} = \begin{bmatrix} 1 & 0 \\ \frac{1}{2} & \frac{\sqrt{3}}{2} \end{bmatrix} a; \quad sc : \mathbf{a} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} a;$$

$$fcc : \mathbf{a} = \begin{bmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{bmatrix} \frac{a}{2}; \quad bcc : \mathbf{a} = \begin{bmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ -1 & 1 & 1 \end{bmatrix} \frac{a}{2}.$$

# Periodic Functions and the Reciprocal Lattice

Consider any function  $f(\mathbf{r})$  defined for the crystal, such as the density of the electrons. This function is the same in each unit cell,

$$f(\mathbf{r} + \mathbf{T}(n_1, n_2, n_3)) = f(\mathbf{r}), \quad (2)$$

where  $\mathbf{T}$  is any translation defined above.

## Fourier transforms

A periodic function can be easily represented by Fourier transforms. The formulas can be written simply in the language of a finite basis if we restrict the Fourier components to only those which are periodic in a large volume of crystal  $\Omega_{crystal}$  composed of  $N_{cell} = N_1 \times N_2 \times \dots$  cells,

$$\exp(i\mathbf{q} \cdot \mathbf{r}) = \exp(i\mathbf{q} \cdot (\mathbf{r} + \mathbf{T}(N_1, N_2, \dots))) \quad (3)$$

so that the vectors  $\mathbf{q}$  are restricted to  $\mathbf{q} \cdot \mathbf{a}_i = \frac{2\pi \text{integer}}{N_i}$ . We will take the limit of large volumes  $\Omega_{crystal}$  so that the final results will be independent of the choice. The Fourier transform is defined to be

$$f(\mathbf{q}) = \frac{1}{\Omega_{crystal}} \int_{\Omega_{crystal}} f(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \quad (4)$$

Since  $f$  is periodic, this can be written:

$$\begin{aligned} f(\mathbf{q}) &= \frac{1}{\Omega_{crystal}} \sum_{n_1, n_2, n_3} \int_{\Omega_{cell}} f(\mathbf{r}) \exp(i\mathbf{q} \cdot (\mathbf{r} + \mathbf{T}(n_1, n_2, n_3))) d\mathbf{r} \\ &= \frac{1}{N_{cell}} \sum_{n_1, n_2, n_3} \exp(i\mathbf{q} \cdot \mathbf{T}(n_1, n_2, n_3)) \times \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} f(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \quad (5) \end{aligned}$$

Now the first term on the right hand side is 0 all  $\mathbf{q}$  except those for which  $\mathbf{q} \cdot \mathbf{T}(n_1, n_2, n_3) = 2\pi \times \text{integer}$  for all translations  $\mathbf{T}$ . Since  $\mathbf{T}(n_1, n_2, n_3)$  is an integral multiple of the primitive translations  $\mathbf{a}_i$ , it follows that  $\mathbf{q} \cdot \mathbf{a}_i = 2\pi \times \text{integer}$ . This defines the Reciprocal Lattice.

## The Reciprocal Lattice

If we define the vectors  $\mathbf{b}_i$ ,  $i = 1, 2, 3$  which are reciprocal to the primitive translations  $\mathbf{a}_i$ , i.e.,

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \quad (6)$$

then the only non-zero Fourier components of  $f(\mathbf{r})$  are for  $\mathbf{q} = \mathbf{G}$ , where the  $\mathbf{G}$  vectors are a lattice of points in reciprocal space defined by

$$\mathbf{G}(n_1, n_2, n_3) = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3. \quad (7)$$

Finally, the non-zero Fourier transform of the periodic function can be written in terms of the integral over one primitive cell,

$$f(\mathbf{G}) = \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} f(\mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{r}) d\mathbf{r} \quad (8)$$

We can also write the definition of the reciprocal lattice vectors in matrix notation

$$\mathbf{b}^T \mathbf{a} = \mathbf{1}; \text{ or } \mathbf{b}^T = \mathbf{a}^{-1} \quad (9)$$

In 3 dimensions there is a geometric interpretation,  $\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|}$ , etc.

It is easy to show that the reciprocal of a square (simple cubic) lattice is also a square (simple cubic) lattice, with dimension  $\frac{2\pi}{a}$ . However, the reciprocal of the triangular lattice is also triangular, but rotated with respect to the crystal lattice,

$$\text{triangular} : \mathbf{b} = \begin{bmatrix} 1 & -\frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} \end{bmatrix} \frac{2\pi}{a}.$$

The bcc and fcc lattices are reciprocal to one another,

$$\text{bcc reciprocal to fcc} : \mathbf{b} = \begin{bmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ -1 & 1 & 1 \end{bmatrix} \frac{2\pi}{a};$$

$$\text{fcc reciprocal to bcc} : \mathbf{b} = \begin{bmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{bmatrix} \frac{2\pi}{a}.$$

# Wigner-Seitz Cell and First Brillouin Zone

The primitive cell for the crystal can be any one of the infinite set of possible choices of cells that fill all space when translated by the set of all lattice vectors. This holds for the direct and the reciprocal lattices.

Is there a way to make a "best" choice that is unique in some important way?

**Wigner-Seitz Cell:** defined to be the most compact cell possible, i.e., the primitive cell around the origin is set of all points closer to the origin than to any other lattice vector. The Wigner-Seitz Cell can always be constructed by the set of points inside the perpendicular bisecting planes between the origin and all other lattice vectors.

**First Brillouin Zone:** the Wigner-Seitz Cell of the reciprocal lattice.

## Basis of Atoms in Primitive Cell

The basis describes the positions of atoms in each unit cell relative to the chosen origin. If there are  $N_{atom}$  atoms per primitive cell, then the basis is specified by the atomic position vectors  $\tau_\kappa$ ,  $\kappa = 1, N_{atom}$ .

NaCl and ZnS are two examples of crystals with an fcc Bravais lattice and a basis of two atoms per cell. For the case of NaCl, one can choose one atom at the origin, since there is inversion symmetry and cubic rotational symmetry around each atomic site:  $\tau_1 = (0, 0, 0)$  and the second basis vector chosen to be  $\tau_2 = (\frac{1}{2}, 0, 0)a$  or any one of the 6 equivalent choices.

The basis for the Zinc Blende structure can be chosen in a symmetric way,  $\tau_1 = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})a$ , and  $\tau_2 = -(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})a$ , which is appropriate for diamond since this is a center of inversion symmetry. One can also choose the origin at one atom, which is a center of tetrahedral symmetry,  $\tau_1 = (0, 0, 0)a$ , and  $\tau_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$  or any of the equivalent choices. (It is easy to show that in terms of the primitive lattice vectors, the  $\tau_2^L = [\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ , etc.

# Excitations and the Bloch Theorem

This follows the "second proof" of the Bloch Theorem in Ashcroft and Mermin.

Excitations of the states of the crystal do not in general have the periodicity of the crystal. We take the Born-Von Karmen boundary conditions that the excitations are required to be periodic in the large volume just as before. In the limit of large volumes, the boundary conditions do not matter.

Consider the eigenstates of any independent particle Schrodinger equation (e.g., Kohn-Sham equations of Density Functional theory),

$$\hat{H}\psi_i(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m_e}\nabla^2 + V(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}). \quad (10)$$

The key point is that  $V(\mathbf{r})$  is periodic since all cells are equivalent.

Now we can use the general properties of solving the Schrodinger equation in a basis, in this case Fourier components or "plane waves". We require that the states be normalized in the volume of the crystal, and any state can be expanded in the complete set of normalized Fourier components,

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{q}} c_{i,\mathbf{q}} \times \frac{1}{\sqrt{\Omega_{crystal}}} \exp(i\mathbf{q} \cdot \mathbf{r}) = \sum_{\mathbf{q}} c_{i,\mathbf{q}} \times |\mathbf{q}\rangle, \quad (11)$$

where the  $c_{i,\mathbf{q}}$  are the expansion coefficients of the wavefunction in the basis  $|\mathbf{q}\rangle$  which are plane waves.

Taking the matrix elements of the terms in the Schrodinger equation, we find

$$\sum_{\mathbf{q}} \langle \mathbf{q}' | \hat{H} | \mathbf{q} \rangle c_{i,\mathbf{q}} = \epsilon_i \sum_{\mathbf{q}} \langle \mathbf{q}' | \mathbf{q} \rangle c_{i,\mathbf{q}} = \epsilon_i c_{i,\mathbf{q}'}. \quad (12)$$

The matrix element of the kinetic energy operator is simply

$$\langle \mathbf{q}' | -\frac{\hbar^2}{2m_e}\nabla^2 | \mathbf{q} \rangle = \frac{\hbar^2}{2m_e} q^2 \delta_{\mathbf{q},\mathbf{q}'}. \quad (13)$$

Since  $V(\mathbf{r})$  is periodic, its matrix elements are given by Eq. (8),

$$\langle \mathbf{q}' | V | \mathbf{q} \rangle = V(\mathbf{G}) \delta_{\mathbf{q}-\mathbf{q}',\mathbf{G}}, \quad (14)$$

where  $\mathbf{G}$  is a reciprocal lattice vector, and

$$V(\mathbf{G}) = \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} V(\mathbf{r}) \exp(i(\mathbf{G} \cdot \mathbf{r})) d\mathbf{r}. \quad (15)$$



# Major Results

**Bands of eigenvalues.** Since the equation above couples only Fourier components which differ by a reciprocal lattice vector, a state labeled by a wavevector  $\mathbf{k}$  in one cell of the reciprocal lattice is completely decoupled from states at any other  $\mathbf{k}'$  in that cell. For each  $\mathbf{k}$  in one cell of the reciprocal lattice, the Fourier components which enter the Schrodinger Eq. are only the set of vectors  $\mathbf{q} = \mathbf{k} + \mathbf{G}$ , where  $\mathbf{G}$  is any of the vectors of the reciprocal lattice. The Hamiltonian may be diagonalized separately for each  $\mathbf{k}$  in one primitive cell. Usually we choose the most compact cell around the origin, called the Brillouin zone. The crystal momentum  $\mathbf{k}$  varies continuously within the primitive cell, and for each  $\mathbf{k}$  there are a discrete set of eigenstates, given by the solution of the matrix equations. This leads to bands of eigenvalues  $\epsilon_{i,\mathbf{k}}$ , and energy gaps where there can be no eigenstates for any  $\mathbf{k}$ .

**The Bloch theorem.** Each eigenfunction labeled by  $i, \mathbf{k}$  can be written as a product of  $\exp(i\mathbf{k} \cdot \mathbf{r}) \times u_{i,\mathbf{k}}(\mathbf{r})$ , where  $u_{i,\mathbf{k}}(\mathbf{r})$  is a periodic function of  $\mathbf{r}$ . This follows since for each  $\mathbf{k}$ , each eigenstates can be written

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}}(\mathbf{G}) \times \frac{1}{\sqrt{\Omega_{crystal}}} \exp(i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}) = \frac{1}{\sqrt{N_{cell}}} \exp(i\mathbf{k} \cdot \mathbf{r}) u_{i,\mathbf{k}}(\mathbf{r}), \quad (16)$$

where

$$u_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}}(\mathbf{G}) \frac{1}{\sqrt{\Omega_{cell}}} \exp(i\mathbf{G} \cdot \mathbf{r}), \quad (17)$$

which is periodic and normalized in one primitive cell.

**The Role of the Brillouin Zone.** The Brillouin zone is unique among all primitive cells because its boundaries are the bisecting planes where Bragg scattering occurs; inside the Brillouin zone there are no such boundaries so that any non-analytic dependence upon  $\mathbf{k}$  can occur only at the boundaries. Thus the boundary points are of special interest.

Examples of Brillouin zones for important cases are shown in a figure given in the Power Point presentation with labels for important symmetry points and lines using the notation of Bouckaret, Smoluchowski, and Wigner.

**Sums over Brillouin Zone** We often need to evaluate quantities like the total density or total energy *per unit cell*. For a function  $f_i(\mathbf{k})$ , where  $i$  denotes the discrete band index, it is straightforward to show from the average value is simply

$$\bar{f}_i = \frac{1}{N_k} \sum_{\mathbf{k}} f_i(\mathbf{k}) \rightarrow \frac{\Omega_{cell}}{(2\pi)^d} \int_{BZ} d\mathbf{k} f_i(\mathbf{k}), \quad (18)$$

where  $\Omega_{cell}$  is the volume of a primitive cell in real space and  $\frac{(2\pi)^d}{\Omega_{cell}}$  is the volume of the BZ. [For example, the fact that each band can hold at most one electron (of each spin) is satisfied by this definition.]

A very convenient choice is the regular grid in  $\mathbf{k}$ -space defined by Monkhorst and Pack. The most efficient grid does *not include the  $\mathbf{k} = 0$  point*. [For visualizing these sums it is simpler to use a parallelepiped primitive cell of the reciprocal lattice rather than the BZ, since the points are evenly distributed in the cell.]

# Calculations of Bands in Plane Wave Basis

Using the formulas above we find the matrix equation for the Schrödinger equation in plane waves:

$$\sum_{\mathbf{G}'} H_{\mathbf{k}}(\mathbf{G}, \mathbf{G}') c_{i,\mathbf{k}}(\mathbf{G}') = \epsilon_{i,\mathbf{k}} c_{i,\mathbf{k}}(\mathbf{G}) \quad (19)$$

where

$$H_{\mathbf{k}}(\mathbf{G}, \mathbf{G}') = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + V(\mathbf{G} - \mathbf{G}') \quad (20)$$

This is a hermitian matrix equation in  $\mathbf{G}, \mathbf{G}'$ , and the solution by standard diagonalization techniques leads to the bands of eigenvalues  $\epsilon_{i,\mathbf{k}}$  and the periodic part of their eigenstates  $u_{i,\mathbf{k}}(\mathbf{r})$ .

## Plane Wave Empirical Pseudopotential Calculations

We now have the equations to solve *any* independent particle problem in a crystal.

What is the problem?

- Works only if the number of plane waves is feasible.
  - Only for hydrogen! Core electrons too difficult for other elements!
  - Or if we use pseudopotentials to eliminate core electrons
- Works only if we have a way of getting the potential  $V(\mathbf{r})$  or  $V(\mathbf{G})$ 
  - Density functional theory provides ways to find  $V$  - approximate, but well tested in many classes in many materials
  - Models and Empirical Approximations for  $V$  show us the general character of solutions

# Sum of Spherical Potentials

Often the potential is given by a sum of spherical potentials in real space. This is always true for the bare proton potentials or the bare ionic pseudopotentials. Often it is also a good approximation to take the entire potential as a sum of spherical potentials. An example which is often rather close to the final potential is to assume  $V(\mathbf{r})$  to be a sum of neutral atom potentials. In any case where the potential is a sum of spherical potentials,

$$V(\mathbf{r}) = \sum_{i=1}^{n_{type}} \sum_{j=1}^{n_{atom}(i)} \sum_{\mathbf{T}} V_{atom}^i(|\mathbf{r} - \vec{\tau}_{i,j} - \mathbf{T}|), \quad (21)$$

then the Fourier transform can be written,

$$V(\mathbf{G}) = \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} V(\mathbf{r}) \exp(i(\mathbf{G} \cdot \mathbf{r})) d\mathbf{r} = \sum_{i=1}^{n_{type}} S_i(\mathbf{G}) V_{atom}^i(|\mathbf{G}|), \quad (22)$$

where the **structure factor** for each type of atom is

$$S_i(\mathbf{G}) = \frac{1}{n_{atom}(i)} \sum_{j=1}^{n_{atom}(i)} \exp(i(\mathbf{G} \cdot \vec{\tau}_{i,j})) \quad (23)$$

and the **form factor** for each type of atom is

$$V_{atom}^i(|\mathbf{G}|) = \frac{n_{atom}(i)}{\Omega_{cell}} \int_{all\ space} V_{atom}^i(|\mathbf{r}|) \exp(i(\mathbf{G} \cdot \mathbf{r})) d\mathbf{r}. \quad (24)$$

This is an approximation to the true potential which is not a sum of spherical potentials. However, it is often a good approximation. Furthermore, in the full Kohn-Sham calculations the bare ionic potential due to the rigid spherical nuclei and cores are spherical and this form is used in that case.

# Model Potentials and Empirical Pseudopotentials

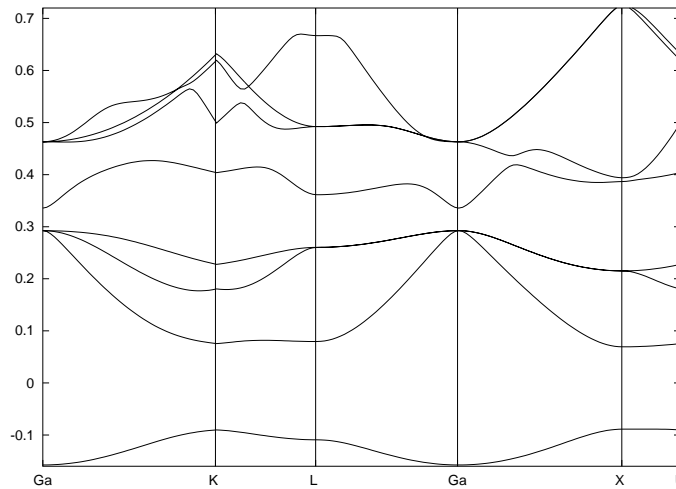
The programs used in our lab exercises use potentials that are sums of spherical atomic-like potentials. These are useful because:

- This is a very good approximation in many cases and gives one a feeling for bands. It is very useful for describing bands, optical properties, etc. See book by Cohen and Chelikowsky.)
- Empirical potentials can be a starting point for large calculations not feasible in *ab initio* methods. Calculations for “quantum dots of many thousands of atoms have been done by Wang, et al (see references) using the same potentials as in our lab.
- Self-consistent *ab initio* calculations also involve terms of exactly the same form in the fixed external potential (nuclei or ions).

The programs used in the lab include empirical potentials for Si, Ga, As, (from S. B. Zhang, et al) and various model cases: “El” (i.e., no potential or “empty lattice”).

Examples of results are shown here:

Figure 1: Bands for GaAs using empirical pseudopotentials



## References

- [1] N. Ashcroft and N. Mermin, *Solid State Physics* (W.B. Saunders Company, New York, 1976).
- [2] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, New York, 1996).
- [3] M. L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors*, 2nd ed. (Springer-Verlag, Berlin, 1988).
- [4] W. E. Pickett, *Computer Physics Reports* **9**, 115 (1989).
- [5] S. B. Zhang, C.-Y. Yeh, and A. Zunger, .
- [6] L.-W. Wang and A. Zunger, *Comp. Mat. Sci.* **2**, 326 (1994).
- [7] L. W. Wang, J. Kim, and A. Zunger, .

Figure 2: Free electron bands for an fcc crystal with the lattice constant of Si.

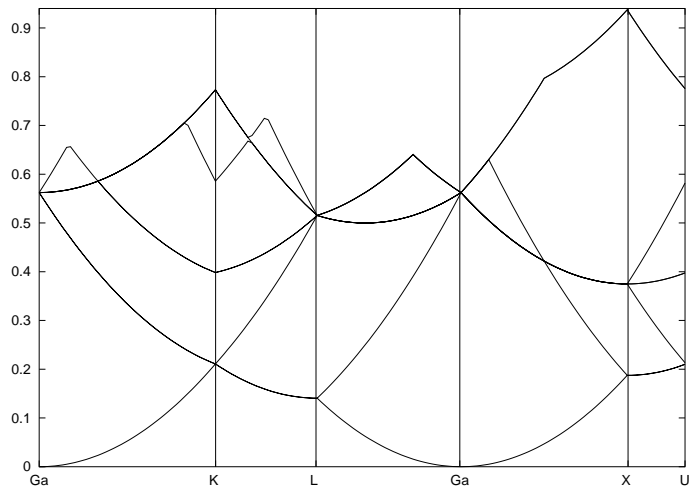


Figure 3: Bands for Si using an empirical pseudopotential

