

# Handout 4

## The tight-binding model

### 4.1 Introduction

In the tight-binding model we assume the opposite limit to that used for the nearly-free-electron approach, *i.e.* the potential is so large that the electrons spend most of their lives bound to ionic cores, only occasionally summoning the quantum-mechanical wherewithal to jump from atom to atom.

The atomic wavefunctions  $\phi_j(\mathbf{r})$  are defined by

$$\mathcal{H}_{\text{at}}\phi_j(\mathbf{r}) = E_j\phi_j(\mathbf{r}), \quad (4.1)$$

where  $\mathcal{H}_{\text{at}}$  is the Hamiltonian of a single atom.

The assumptions of the model are

1. close to each lattice point, the crystal Hamiltonian  $\mathcal{H}$  can be approximated by  $\mathcal{H}_{\text{at}}$ ;
2. the bound levels of  $\mathcal{H}_{\text{at}}$  are well localised, *i.e.* the  $\phi_j(\mathbf{r})$  are very small one lattice spacing away, implying that
3.  $\phi_j(\mathbf{r})$  is quite a good approximation to a stationary state of the crystal, as will be  $\phi_j(\mathbf{r} + \mathbf{T})$ .

Reassured by the second and third assumptions, we make the Bloch functions  $\psi_{j,\mathbf{k}}$  of the electrons in the crystal from linear combinations of the atomic wavefunctions.

### 4.2 Band arising from a single electronic level

A method of obtaining the dispersion relation for a single electronic level  $E_\nu(\mathbf{k})$  in the tight binding approximation was given in lectures. Note that this topic is also covered in a number of textbooks. *Band theory and electronic properties of solids*, by John Singleton (Oxford University Press, 2001) considers the specific case of a crystal with mutually perpendicular (Cartesian) basis vectors, this may help you understand the more general result.

### 4.3 General points about the formation of tight-binding bands

The derivation given in the lecture illustrates several points about real bandstructure.

1. Figure 4.1 shows schematically the process involved in forming the tight-binding bands.  $N$  single atoms with  $p$  (doubly degenerate) atomic levels have become  $p$   $2N$ -fold degenerate bands.
2. The transfer integrals give a direct measure of the width in energy of a band (the *bandwidth*); small transfer integrals will give a narrow bandwidth. In question 2 of [problem set 1](#), we shall see that carriers close to the bottom of a tight-binding band have *effective masses* which are inversely proportional to the transfer integrals. The effective mass parameterises the ease with

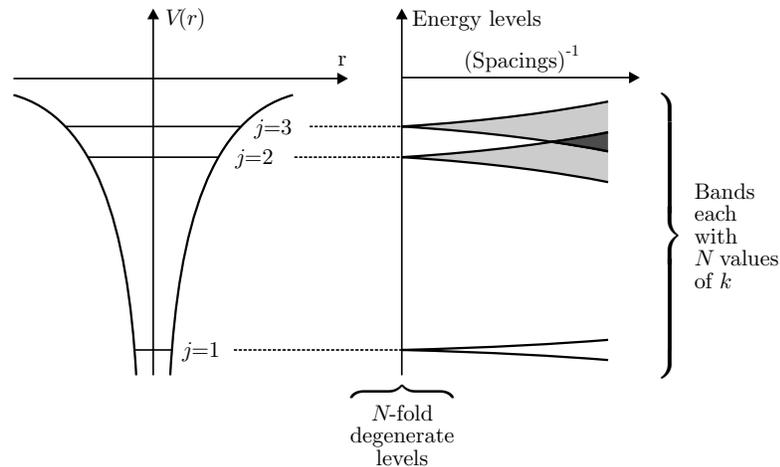


Figure 4.1: Schematic representation of the formation of tight-binding bands as the spacing between atoms is reduced.

which an electron can be accelerated. Thus, small transfer integrals lead to heavy effective masses (and narrow bandwidths), indicating that it is hard to move the electrons around; large transfer integrals lead to light effective masses (and large bandwidths), indicating that it is easy to move the electrons around. This ties in exactly with the real-space picture of the formation of tight-binding bands, in which the transfer integrals reflect the ease with which an electron can transfer from atom to atom.

3. The “shape” of the bands in  $k$ -space will be determined in part by the real-space crystal structure; if the atoms in a certain direction are far apart, then the bandwidth will be narrow for motion in that direction.
4. The bands will also reflect the character of the atomic levels which have gone to make them up.

The latter point will be illustrated in Section 4.3.1 below.

### 4.3.1 An example: the transition metals

The tight-binding model implies that bands will reflect the character of the atomic levels which have gone to make them up. This is illustrated by Figure 4.2, which shows the calculated tight-binding bands for Copper. Note that the character of the original atomic levels is reflected in the width and shape of the the bands; the more compact and anisotropic 3d orbitals give rise to five narrow bands of complex shape, whilst the single band derived from the larger, spherical 4s orbitals is wide and almost free-electron-like. The properties of a particular 3d metal are strongly dependent on the position of the Fermi energy amongst this mess.

Note that the colours of 3d metals such as Cu and Au result from the optical transitions which are possible between the occupied d-bands and the empty states at the top of the s-band.

## 4.4 Reading

Alternative treatments are given in *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) Chapter 9 (simpler), *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) Section 10.9 (see also Section 10.3) (simpler), *Band theory and electronic properties of solids*, by John Singleton (Oxford University Press, 2001) Chapter 4 (same level, more details) and *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) pages 176-190 (more general and therefore more complicated). The tight-binding model is related to the



*Kronig-Penney Model*, which is a very simple illustration of the formation of bands; see *e.g.* *Quantum Mechanics*, by Stephen Gasiorowicz (Wiley, New York 1974) page 98.