The Tight Binding Method

Mervyn Roy

May 7, 2015

The tight binding or linear combination of atomic orbitals (LCAO) method is a semi-empirical method that is primarily used to calculate the band structure and single-particle Bloch states of a material. The semi-empirical tight binding method is simple and computationally very fast. It therefore tends to be used in calculations of very large systems, with more than around a few thousand atoms in the unit cell.

1   Background: a hierarchy of methods

When the number of atoms and electrons is very small we can use an exact method like configuration interaction to calculate the true many-electron wavefunction. However, beyond about 10-electrons we hit the *exponential wall* and such calculations become impossible.

For larger systems containing up to a few hundred or a few thousand atoms we can use density functional theory (DFT) techniques to find the true ground state density and ground state energy of the interacting system without explicitly calculating the many-electron wavefunction. In a DFT calculation we calculate approximate single-particle energies that, in practice, often give a reasonable approximation to the actual band structure of the crystal.

In even larger systems, with around 10,000 or more atoms, we can no longer use self-consistent DFT calculations to take into account the full interaction. To calculate the band structure and a set of approximate single particle states we instead try to include the effects of the interaction in a semi-empirical way, using parameters that we can adjust to match experiment.

The starting point for all semi-empirical approaches is the physics. In metals, for example, the electrons are almost free and so we can treat the single

particle states in terms of plane waves (leading to the Central equation, and nearly free electron theory). We could also take a very different approach and assume the states in a crystal look like combinations of the wavefunctions of isolated atoms. We might imagine this is more likely to be the case in insulators or semiconductors.

Here, we will solve the single particle Schrödinger equation for the states in a crystal by expanding the Bloch states in terms of a linear combination of atomic orbitals.

2 Linear combination of atomic orbitals

2.1 Crystal and atomic hamiltonians

In a crystal, we take the single particle hamiltonian to be

$$H = H_{at} + \Delta U, \tag{1}$$

where H_{at} is the hamiltonian for a single atom and ΔU encodes all the differences between the true potential in the crystal and the potential of an isolated atom. We assume $\Delta U \to 0$ at the centre of each atom in the crystal.

The single particle states in the crystal are then $\psi_{n\mathbf{k}}(\mathbf{r})$, where

$$H\psi_{n\mathbf{k}}(\mathbf{r}) = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}), \tag{2}$$

the band index is labelled by n, and $\mathbf{k}$ is a wavevector in the first Brillouin zone.

2.2 The atomic wavefunctions

The atomic wavefunctions, $\phi_i(\mathbf{r})$ are eigenstates of H_{at},

$$H_{at}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \tag{3}$$

where ϵ_i is the energy of the i energy level in an isolated atom. These wavefunctions decay rapidly away from $\mathbf{r} = 0$ and so the *overlap* integral, $\gamma(|\mathbf{R}|) = \int \phi_i^*(\mathbf{r})H\phi_i(\mathbf{r} + \mathbf{R})d\mathbf{r}$, between wavefunctions located on separate atomic sites ($\mathbf{R} \neq 0$) in the crystal is small (see Fig. 1).

Throughout these notes we will use orthonormal atomic orbitals that have zero direct overlap between different lattice sites,

$$\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r} + \mathbf{R})d\mathbf{r} = \begin{cases} 1 & \text{if } i = j \text{ and } \mathbf{R} = 0 \\ 0 & \text{otherwise.} \end{cases} \tag{4}$$

This gives a simple *orthogonal* tight-binding formalism but it is relatively easy to generalise from this to more complex forms.
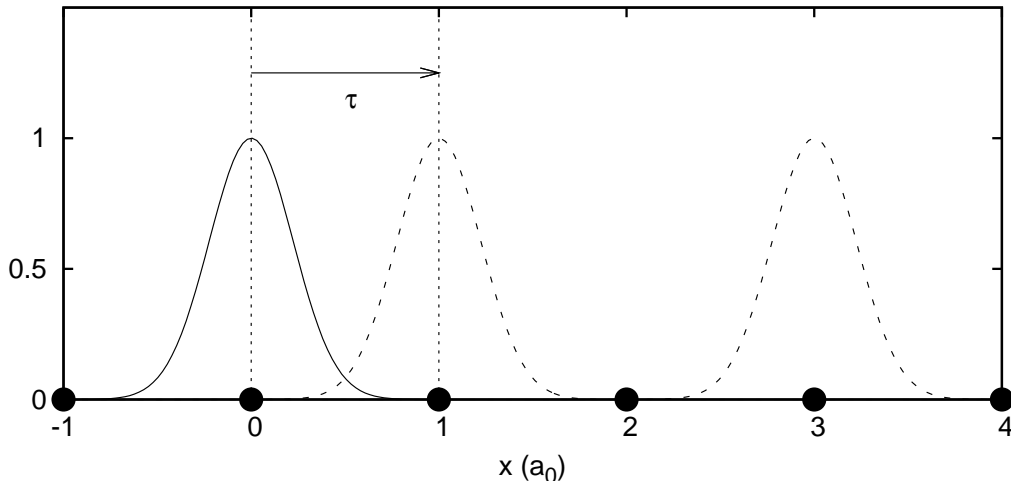

Figure 1: Schematic of the atomic orbitals in a 1D crystal with atoms separated by a_0. The translation vectors are $\mathbf{R} = 0, \pm a_0\mathbf{i}, \pm 2a_0\mathbf{i}, \pm 3a_0\mathbf{i}, \ldots$, where $\mathbf{i}$ is a unit vector in the x direction. One of the nearest neighbour vectors $\boldsymbol{\tau} = a_0\mathbf{i}$ is shown in the diagram and the vertical dotted lines denote the edges of the unit cell which contains a single atom. The solid curve shows an example atomic orbital centred on an atom at $\mathbf{r} = 0$, while dashed lines show orbitals centred on $\mathbf{r} + \boldsymbol{\tau}$ and $\mathbf{r} + 3\boldsymbol{\tau}$. The orbitals decay rapidly so the overlap, $\phi_i^*(\mathbf{r})\phi_i(\mathbf{r} + \mathbf{R})$, is small. Here we assume the overlap integral, $\int \phi_i^*(\mathbf{r})H\phi_i(\mathbf{r} + \mathbf{R})d\mathbf{r}$, is only significant when $|\mathbf{R}|$ is close to the near-neighbour separation $|\boldsymbol{\tau}|$, and that the direct overlap between orbitals on different lattice sites is zero (see Eq. (4)).

2.3 Bloch's theorem

The single particle states must obey Bloch's theorem,

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r}), \tag{5}$$

where $\mathbf{R}$ is a real space translation vector of the crystal.

Clearly, a single atomic orbital does not satisfy Bloch's theorem, but we can easily make a linear combination of atomic orbitals that does,

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r} - \mathbf{R}), \tag{6}$$

where there are N lattice sites in the crystal and the factor of $1/\sqrt{N}$ ensures the Bloch state is normalised (see appendix A).

2.3.1 Proof that $\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r} - \mathbf{R})$ satisfies Bloch's theorem

If $\mathbf{R}'$ is a real space translation vector and $\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r} - \mathbf{R})$ then,

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}') \;\; = \;\; \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r} - (\mathbf{R} - \mathbf{R}')).$$

But, $\mathbf{R} - \mathbf{R}' = \mathbf{R}''$ is simply another crystal translation vector and, because the sum over $\mathbf{R}$ goes over all of the translation vectors in the crystal, we can replace it by another equivalent translation vector, $\mathbf{R}''$. Then, substituting for $\mathbf{R} = \mathbf{R}' + \mathbf{R}''$ in the complex exponential we have

$$
\begin{aligned}
\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}') \;\; &= \;\; \frac{1}{\sqrt{N}} \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot(\mathbf{R}'+\mathbf{R}'')} \phi_n(\mathbf{r} - (\mathbf{R}'')), \\
&= \;\; e^{i\mathbf{k}\cdot\mathbf{R}'} \frac{1}{\sqrt{N}} \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot\mathbf{R}''} \phi_n(\mathbf{r} - (\mathbf{R}'')), \\
&= \;\; e^{i\mathbf{k}\cdot\mathbf{R}'} \psi_{n\mathbf{k}}(\mathbf{r}),
\end{aligned}
$$

so that the $\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r} - \mathbf{R})/\sqrt{N}$ from Eq. (6) satisfies Bloch's theorem (Eq. (5)).

3 Calculation of the band structure

3.1 Single s-band

Imagine a crystal with translation vectors $\mathbf{R}$, that has one atom in the unit cell, and where only atomic s-orbitals $\phi_s(\mathbf{r})$ contribute to the crystal states. Then there is only 1 band ($n = 1$) and there is only one Bloch state we can construct,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_s(\mathbf{r} - \mathbf{R}). \tag{7}$$

In this simple case we can find the dispersion relation (the relation between energy and wavevector) simply by calculating the expectation value of the energy,

$$E(\mathbf{k}) = \int \psi_{\mathbf{k}}^*(\mathbf{r}) H \psi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r}, \tag{8}$$

where the integrals are over all space. Then, substituting for $\psi_{\mathbf{k}}(\mathbf{r})$ from Eq. (7) we find,

$$
\begin{aligned}
E(\mathbf{k}) &= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \int \phi_s^*(\mathbf{r}-\mathbf{R}) H \phi_s(\mathbf{r}-\mathbf{R}') d\mathbf{r} \\
&= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x}-(\mathbf{R}'-\mathbf{R})) d\mathbf{x}, \quad (9)
\end{aligned}
$$

where in the last step we have changed variable from $\mathbf{r}$ to $\mathbf{x} = \mathbf{r}-\mathbf{R}$ and H is unchanged because it has the periodicity of the lattice (ie. $H(\mathbf{r}) = H(\mathbf{r}-\mathbf{R})$).

Now, in Eq.(9), for each particular $\mathbf{R}$ in the sum, $\mathbf{R}' - \mathbf{R} = \mathbf{R}''$ is just another fixed translation vector. Because the sum over $\mathbf{R}'$ goes over all translation vectors we will get the same result by summing over another translation vector, $\mathbf{R}''$. Substituting for $\mathbf{R}''$ we therefore have,

$$
E(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot\mathbf{R}''} \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x}-\mathbf{R}'') d\mathbf{x},
$$

and, because each of the terms in the sum over $\mathbf{R}$ is now identical, this sum simply gives us a factor of N, one term for each of the N possible values of R. Then,

$$
E(\mathbf{k}) = \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot\mathbf{R}''} \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x}-\mathbf{R}'') d\mathbf{x}. \quad (10)
$$

We can now separate out different terms in the sum over $\mathbf{R}''$ by considering the range of the atomic s-orbitals, $\phi_s(\mathbf{r})$. The atomic orbitals are tightly localised: they are large when $|\mathbf{r}|$ is small and decay rapidly away from $\mathbf{r} = 0$.

First, if $\mathbf{R}'' = 0$ then the integral in Eq. (10) becomes

$$
\int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x}) d\mathbf{x} = \int \phi_s^*(\mathbf{x}) \epsilon_s \phi_s(\mathbf{x}) d\mathbf{x} = \epsilon_s, \quad (11)
$$

because $H\phi_s(\mathbf{x}) = \epsilon_s \phi_s(\mathbf{x})$ and the atomic states $\phi_s(\mathbf{x})$ are normalised. So, the $\mathbf{R}'' = 0$ simply gives ϵ_s, the energy of the atomic s-orbital in an isolated atom.

Next, if $|\mathbf{R}''|$ is large we expect that the integral $\int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x}-\mathbf{R}'') d\mathbf{x} \approx 0$ because the *overlap* between wavefunctions separated by large $\mathbf{R}''$ is very small. Typically, in a semi-empirical tight binding calculation we therefore only include terms where $|\mathbf{R}''|$ is small, for example if $\mathbf{R}'' = \boldsymbol{\tau}$ is the

translation vector between an atom and its nearest neighbours (see Fig. 1). Then,

$$E(\mathbf{k}) = \epsilon_s + \sum_{\boldsymbol{\tau}} e^{i\mathbf{k}\cdot\boldsymbol{\tau}} \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x} - \boldsymbol{\tau}) d\mathbf{x}. \tag{12}$$

Finally, in an empirical tight binding calculation we do not attempt to evaluate the overlap integral, $\int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x} - \boldsymbol{\tau}) d\mathbf{x}$ explicitly. Instead we replace it with a parameter, γ, whose value we adjust to match experiment,

$$\gamma(|\boldsymbol{\tau}|) = \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x} - \boldsymbol{\tau}) d\mathbf{x}, \tag{13}$$

so that,

$$E(\mathbf{k}) = \epsilon_s + \sum_{\boldsymbol{\tau}} e^{i\mathbf{k}\cdot\boldsymbol{\tau}} \gamma(|\boldsymbol{\tau}|). \tag{14}$$

Often empirical relations are also used to scale the overlap integrals with the separation $|\boldsymbol{\tau}|$. For example, in silicon the relation $\gamma(|\boldsymbol{\tau}|) = A e^{-\alpha|\boldsymbol{\tau}|^2}/|\boldsymbol{\tau}|^2$ gives the approximate scaling of the overlap integral with near neighbour separation $|\boldsymbol{\tau}|$. By using approximate scaling relations, we can investigate the effect on the band structure of straining or deforming a crystal.

3.2 Single s-band in a 1D crystal

In a 1D crystal the translation vectors are $\mathbf{R} = n a_0 \mathbf{i}$ where n is an integer, a_0 is the atomic separation and $\mathbf{i}$ is a unit vector in the x-direction. In this case there are two nearest neighbour translation vectors $\boldsymbol{\tau} = \pm a_0 \mathbf{i}$.

Then, if $\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_s(\mathbf{r} - \mathbf{R})$,

$$
\begin{aligned}
E(\mathbf{k}) &= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \int \phi_s^*(\mathbf{r} - \mathbf{R}) H \phi_s(\mathbf{r} - \mathbf{R}') d\mathbf{r}, \\
&= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x} - (\mathbf{R}' - \mathbf{R})) d\mathbf{x}, \\
&= \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot\mathbf{R}''} \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x} - \mathbf{R}'') d\mathbf{x}, \\
&= \epsilon_s + \sum_{\boldsymbol{\tau}} e^{i\mathbf{k}\cdot\boldsymbol{\tau}} \gamma(|\boldsymbol{\tau}|),
\end{aligned}
$$

Where we have calculated the expectation value of the energy (line 1) through the following steps,

1. In line 2 we change variable from $\mathbf{r}$ to $\mathbf{x} = \mathbf{r} - \mathbf{R}$.

6

2. In line 3 we replace $\mathbf{R}' - \mathbf{R}$ with a translation vector $\mathbf{R}'' = \mathbf{R}' - \mathbf{R}$ that we can equally well sum over. Once we do this, we recognise that the sum over $\mathbf{R}$ simply gives a factor of N.

3. Finally, we separate off the $\mathbf{R}'' = 0$ term (which gives the atomic energy, ϵ_s), restrict the remaining terms in the sum to nearest neighbours $\boldsymbol{\tau}$, and replace the overlap integral with some numerical parameter, γ.

In a 1D crystal we know that $\boldsymbol{\tau} = \pm a_0 \mathbf{i}$ and that the only meaningful wavevectors, $\mathbf{k}$, must also be in the direction of $\mathbf{i}$, so that $\mathbf{k} = k\mathbf{i}$. Then,

$$
\begin{aligned}
E(k) &= \epsilon_s + \gamma(a_0)\left(e^{ika_0} + e^{-ika_0}\right) \\
&= \epsilon_s + 2\gamma(a_0)\cos(ka_0).
\end{aligned} \tag{15}
$$

This is the dispersion relation for a single s-band in a 1D crystal. It describes how the energy varies with crystal momentum, k. It also tells us the *bandwidth* (see Fig. 2).

In the 1D crystal the length of the unit cell in real space is a_0, so the length of the unit cell in reciprocal space is $2\pi/a_0$. In figure 2 we plot $E(k)$ inside the unit cell in reciprocal space, from $k = 0$ to $k = 2\pi/a_0$. At large k the dispersion relation simply repeats.[1] The *bandwidth*, 4γ, is marked on the plot. This is the difference between the maximum and minimum allowed energy of the band.
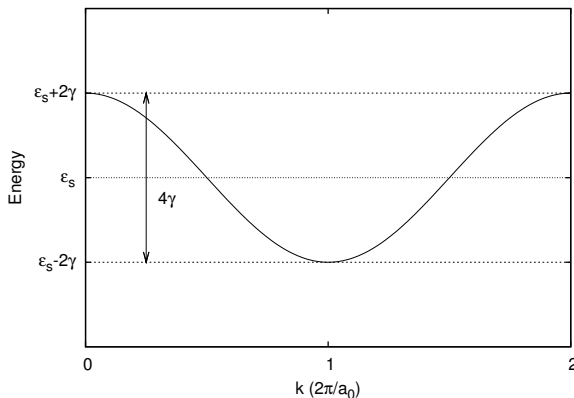

Figure 2: The $E(k)$ relation for a single s-band in a 1D crystal. The k range is 0 to $2\pi/a_0$. The bandwidth 4γ is marked on the plot.

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[1]Usually we would plot $E(k)$ within the first Brillouin zone (BZ). This is an equivalent cell (the Wigner-Seitz cell) in reciprocal space. The BZ length is still $2\pi/a_0$ but the BZ extends from $-\pi/a_0$ to π/a_0 rather than 0 to $2\pi/a_0$.

3.3   s-band in a 2D crystal

A simple 2D rectangular crystal is shown in Fig. 3 (left). If s-orbitals from each atom contribute to the states of the crystal we again have that

$$E(\mathbf{k}) = \epsilon_s + \sum_{\boldsymbol{\tau}} e^{i\mathbf{k}\cdot\boldsymbol{\tau}}\gamma(|\boldsymbol{\tau}|),$$

but now there are 4 vectors: $\boldsymbol{\tau} = \pm a\mathbf{i}$ and $\boldsymbol{\tau} = \pm b\mathbf{j}$ that take us to nearby atoms where the overlap integral might be significant. The wavevector $\mathbf{k}$ can also vary in both x and y directions, $\mathbf{k} = k_x\mathbf{i} + k_y\mathbf{j}$. Then,

$$E(k_x, k_y) = \epsilon_s + 2\gamma(a)\cos(k_x a) + 2\gamma(b)\cos(k_y b). \tag{16}$$

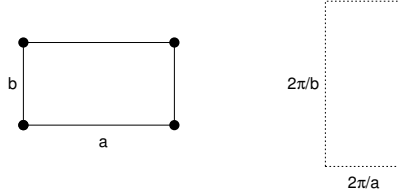We can plot the dispersion relation as a function of k_x and k_y within one

Figure 3: Left: unit cell of an example rectangular 2D crystal in real space, where filled circles label the atom positions. Right: unit cell in reciprocal space.

unit cell in reciprocal space (see Fig. 4). The cell lengths are $2\pi/a$ and $2\pi/b$ (see Fig. 3) and the BZ extends from $-\pi/a$ to π/a and $-\pi/b$ to π/b. The bandwidth is $4\gamma(a) + 4\gamma(b)$.
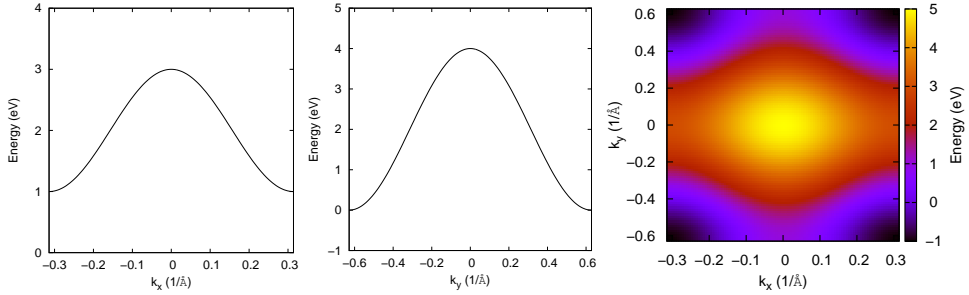

Figure 4: Example dispersion relation $E(k_x, k_y)$ for a 2D crystal with $a = 10$ Å, $b = 5$ Å, $\gamma(a) = 0.5$ eV, $\gamma(b) = 1$ eV and $\epsilon_s = 2$ eV. Left panel: $E(k_x, \pi/2b)$. Centre: $E(\pi/2a, k_y)$. Right: Colour map of the full 2D dispersion relation $E(k_x, k_y)$ within the first BZ. In this case the bandwidth is $4\gamma(a) + 4\gamma(b) = 6$ eV.

3.4 s-band in a 3D crystal

Generalising to 3D is now very easy. We still have $E(\mathbf{k}) = \epsilon_s + \sum_{\boldsymbol{\tau}} e^{i\mathbf{k}\cdot\boldsymbol{\tau}} \gamma(|\boldsymbol{\tau}|)$ but now $\mathbf{k} = (k_x, k_y, k_z)$ and $\boldsymbol{\tau}$ will, in general, have $x, y,$ and z components. For example, in a face centred cubic crystal the 12 nearest neighbour vectors are $\boldsymbol{\tau} = (\pm 1, \pm 1, 0)a/2, (\pm 1, 0, \pm 1)a/2, (0, \pm 1, \pm 1)a/2$. With a little algebra this eventually gives

$$
\begin{aligned}
E(k_x, k_y, k_z) &= \epsilon_s + 4\gamma(|\boldsymbol{\tau}|) \left(\cos\frac{k_x a}{2} \cos\frac{k_y a}{2} + \right. \\
&\left. \cos\frac{k_y a}{2} \cos\frac{k_z a}{2} + \cos\frac{k_z a}{2} \cos\frac{k_x a}{2} \right),
\end{aligned}
\tag{17}
$$

where $|\boldsymbol{\tau}| = a/\sqrt{2}$.

3.5 The effect of adjusting the overlap integral, γ.

The γ parameter controls the bandwidth and the curvature of the bands. We can adjust γ to match experiment. Or, if we know how γ scales with, for example, atomic separation, we can see how the bandwidth will change when we strain the crystal. Figure 5 shows the dispersion relation $E(\pi/2a, k_y)$ from Eq. (16) for 3 different values of $\gamma(b)$. As $\gamma(b)$ decreases, the bandwidth and the curvature of the band also decrease. The effective mass is inversely proportional to the curvature so, if γ is small the relevant effective masses tend to be large.
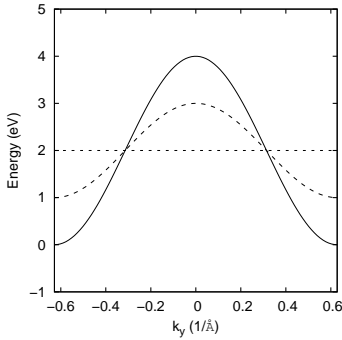

Figure 5: The dispersion relation for a 2D rectangular lattice, $E(k_x, k_y) = \epsilon_s + 2\gamma(a)\cos(k_x a) + 2\gamma(b)\cos(k_y b)$, plotted as a function of k_y at $k_x = \pi a/2$. In this example 2D crystal, $a = 10$ Å, $b = 5$ Å, $\gamma(a) = 0.5$ eV, and $\epsilon_s = 2$ eV. Solid line: $\gamma(b) = 1$ eV. Long dashed line: $\gamma(b) = 0.5$ eV. Dotted line: $\gamma(b) = 0$ eV.

3.6 The origin of bands

Now that we have seen how the bandwidth scales with the overlap integral, γ, we can gain some insight into the origin of the bands in a crystal.

Figure 6 shows a schematic illustrating the origin of bands in a tight binding picture. In an isolated atom we have a set of individual atomic levels, for example, 1s, 2s, 2p etc. In a crystal with N atoms and zero overlap between atomic states we would therefore have N degenerate levels for each atomic state. As the overlap integral increases these levels broaden into bands, each containing N different allowed $\mathbf{k}$ values.
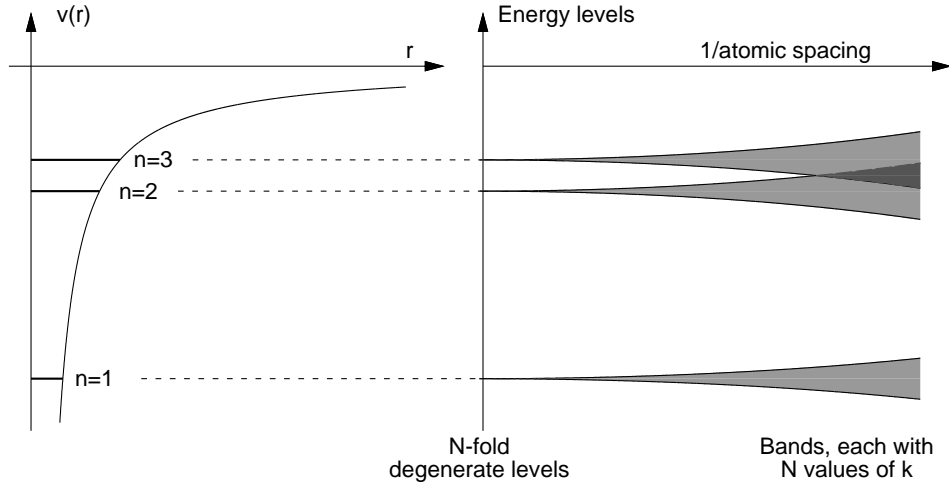

Figure 6: Schematic diagram illustrating the origin of bands in a tight binding picture. Left: the undegenerate electronic levels in a single atom. Right: energy levels for the N atoms in a crystal, plotted as a function of overlap integral or the inverse of the atomic spacing. Reproduced from *Solid State Physics*, N.W. Ashcroft and N.D. Mermin, Holt Saunders International edition (1981).

3.7 N_b-atom basis

In general, a material will have more than one atom in the unit cell and, in modern applications, the tight-binding method only comes into its own when there are a very large number of atoms in the unit cell.

The chain molecule *trans*-polyacetylene shown in Fig. 7 is an example of a material with 2 atoms in the unit cell.

In a crystal with an N_b atom basis (and where only one type of atomic orbital contributes to the band states) we can make N_b linear combinations of atomic orbitals that satisfy Bloch's theorem,

$$\Phi_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_i} e^{i\mathbf{k}\cdot\mathbf{R}_i} \phi(\mathbf{r} - \mathbf{R}_i). \tag{18}$$
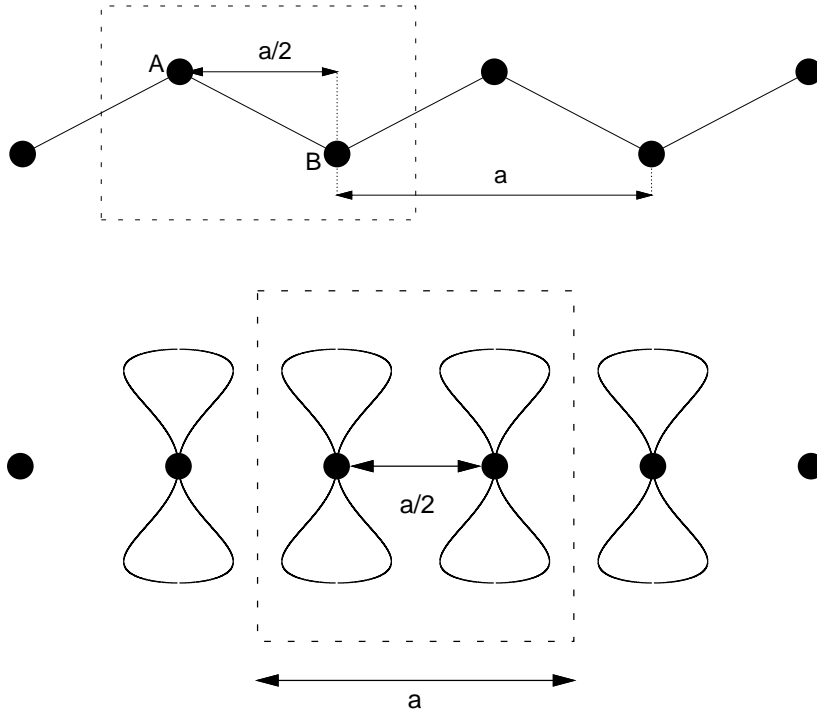
Figure 7:   *Trans*-polyacetylene. Top: plan view, with the two non-identical atom sites in the basis labelled A and B. Bottom: side view showing a schematic of the p_z orbitals located on the central 4 atoms. The filled black circles label the carbon atoms and the boxes denoted with a dashed line show the unit cell. The unit cell contains two atoms, one at $(0,0)$ and one at $\mathbf{R}_{AB} = (a/2, a/2\sqrt{3})$.

The $i = 1, 2, \ldots, N_b$ label each of the different atoms in the basis and the $\mathbf{R}_i$ are translation vectors that take us between atoms of type i. For example, in *trans*-polyacetylene (see Fig. 7) i would label an A or a B atom, and the translation vectors would be $\mathbf{R}_A = \pm a\mathbf{i}, \pm 2a\mathbf{i}, \ldots$ with $\mathbf{R}_B = \mathbf{R}_{AB} \pm a\mathbf{i}, \mathbf{R}_{AB} \pm 2a\mathbf{i}, \ldots$, where $\mathbf{R}_{AB}$ is a vector between the A and B lattice sites in the basis, and, as before, $\mathbf{i}$ and $\mathbf{j}$ are unit vectors in the x and y directions.

The crystal states can be expanded as a linear combination of the N_b Bloch states,

$$\begin{aligned}
\psi_{n\mathbf{k}}(\mathbf{r}) &= \sum_i c_{i\mathbf{k}} \Phi_{i\mathbf{k}}(\mathbf{r}) \\
&= \sum_i c_{i\mathbf{k}} \sum_{\mathbf{R}_i} e^{i\mathbf{k}\cdot\mathbf{R}_i} \phi(\mathbf{r} - \mathbf{R}_i)/\sqrt{N}.
\end{aligned} \tag{19}$$

From the variational theorem, the best set of states we can find are the ones with the lowest energy. So, to find the $\psi_{n\mathbf{k}}$, we must minimise the expectation value of the energy with respect to the coefficients, $c_{i\mathbf{k}}$. This

is a standard procedure (see for example the notes on quantum chemistry) that leads to the following set of simultaneous equations,

$$\sum_i \left(H_{ij} - \delta_{ij} E(\mathbf{k}) \right) c_{j\mathbf{k}} = 0, \tag{20}$$

where $H_{ij} = \langle \Phi_{i\mathbf{k}} | H | \Phi_{j\mathbf{k}} \rangle$. This only has non-trivial solutions if the determinant,

$$|\mathbf{H} - E(\mathbf{k})\mathbf{I}| = 0, \tag{21}$$

where $\mathbf{H}$ is a matrix of elements, H_{ij}, and $\mathbf{I}$ is the unit matrix.

3.7.1 2-atom basis

When $N_b = 2$ the solution of Eq. (21) is simple. We have,

$$\begin{vmatrix} H_{\mathrm{AA}} - E & H_{\mathrm{AB}} \\ H_{\mathrm{BA}} & H_{\mathrm{BB}} - E \end{vmatrix} = 0, \tag{22}$$

where $H_{\mathrm{AB}} = H_{\mathrm{BA}}^*$. This is a simple quadratic equation with two solutions,

$$E(\mathbf{k}) = -\frac{1}{2}(H_{\mathrm{AA}} + H_{\mathrm{BB}}) \pm \sqrt{\frac{1}{4}(H_{\mathrm{AA}} - H_{\mathrm{BB}})^2 + |H_{\mathrm{AB}}|^2}. \tag{23}$$

With two atoms in the unit cell we get 2 valid solutions at each $\mathbf{k}$. This means two bands.

We can calculate the hamiltonian matrix elements in essentially the same way as we did for the single s-band. For example, in *trans*-polyacetylene (see Fig. 7) each carbon atom contribute a single p-orbital (of energy $\epsilon - p$) to the conduction and valence bands. In this case we have,

$$\begin{aligned} H_{\mathrm{AA}} &= \frac{1}{N} \sum_{\mathbf{R}_\mathrm{A}} \sum_{\mathbf{R}'_\mathrm{A}} e^{i\mathbf{k}\cdot(\mathbf{R}'_\mathrm{A} - \mathbf{R}_\mathrm{A})} \int \phi_s^*(\mathbf{r} - \mathbf{R}_\mathrm{A}) H \phi_s(\mathbf{r} - \mathbf{R}'_\mathrm{A}) d\mathbf{r}, \\ &= \sum_{\mathbf{R}_\mathrm{A}''} e^{i\mathbf{k}\cdot\mathbf{R}_\mathrm{A}''} \int \phi_s^*(\mathbf{x}) H \phi_s(\mathbf{x} - \mathbf{R}_\mathrm{A}'') d\mathbf{x}, \\ &= \epsilon_p + \sum_{m \neq 0} e^{imka} \gamma(|ma|), \end{aligned} \tag{24}$$

where m is an integer that can be positive or negative, k is the magnitude of $\mathbf{k}$ in the x-direction and, in the last step, we have explicitly substituted for the translation vectors $\mathbf{R}_\mathrm{A} = ma\mathbf{i}$.

By following the same procedure we can find an identical result for H_{BB}.

Next, for simplicity we look at a case where the overlap integrals fall off quickly with distance[2], and restrict the overlap integrals to distances $\leq a$. Then $\gamma(ma) = 0$ for $|m| > 1$, and we simply have that,

$$H_{\mathrm{AA}} = H_{\mathrm{BB}} = \epsilon_p + 2\gamma(a)\cos(ka). \tag{25}$$

We follow the same procedure to calculate H_{AB},

$$
\begin{aligned}
H_{\mathrm{AB}} &= \frac{1}{N}\sum_{\mathbf{R}_{\mathrm{A}}}\sum_{\mathbf{R}_{\mathrm{B}}} e^{i\mathbf{k}\cdot(\mathbf{R}_{\mathrm{A}}-\mathbf{R}_{\mathrm{B}})}\int \phi_s^*(\mathbf{r}-\mathbf{R}_{\mathrm{A}})H\phi_s(\mathbf{r}-\mathbf{R}_{\mathrm{B}})d\mathbf{r}, \\
&= \sum_{\mathbf{R}_{\mathrm{A}}'} e^{i\mathbf{k}\cdot(\mathbf{R}_{\mathrm{AB}}+\mathbf{R}_{\mathrm{A}}')}\int \phi_s^*(\mathbf{x})H\phi_s(\mathbf{x}-(\mathbf{R}_{\mathrm{AB}}+\mathbf{R}_{\mathrm{A}}'))d\mathbf{x}. \tag{26}
\end{aligned}
$$

We include only overlap integrals between nearest neighbours so that we retain only the $\mathbf{R}_{\mathrm{A}} = 0$, and $\mathbf{R}_{\mathrm{A}} = -a\mathbf{i}$ terms in the sum (see Fig. 7). We can write,

$$H_{\mathrm{AB}} = \sum_{\boldsymbol{\tau}} e^{i\mathbf{k}\cdot\boldsymbol{\tau}}\gamma(|\boldsymbol{\tau}|), \tag{27}$$

where, in our case, the nearest neighbour vectors, $\boldsymbol{\tau}$ are simply $\boldsymbol{\tau} = \mathbf{R}_{\mathrm{AB}} = (a/2, a/2\sqrt{3})$ and $\boldsymbol{\tau} = \mathbf{R}_{\mathrm{AB}} - a\mathbf{i} = (-a/2, a/2\sqrt{3})$. Again, because *trans*-polyacetylene is a one dimensional crystal, $\mathbf{k}$ is in the x-direction and,

$$
\begin{aligned}
H_{\mathrm{AB}} &= \left(e^{ika/2} + e^{-ika/2}\right)\gamma(|\boldsymbol{\tau}|), \\
&= 2\cos(ka/2)\gamma(|\boldsymbol{\tau}|). \tag{28}
\end{aligned}
$$

Using the results for H_{AA}, H_{BB}, and H_{AB} we can explicitly calculate the dispersion relation from Eq. (23). In *trans*-polyacetylene,

$$E(k) = \epsilon_p + 2\gamma(a)\cos(ka) \pm 2\cos(ka/2)\gamma(|\boldsymbol{\tau}|). \tag{29}$$

This dispersion relation is plotted in Fig. 8. The figure shows two different possible dispersion relations, calculated with different γ parameters.

The famous graphene band structure near the Dirac point can be obtained from an approach almost identical to that used for *trans*-polyacetylene. The main difference is that graphene is a 2-dimensional crystal so $\mathbf{k}$ and the real space lattice vectors vary in both x and y directions.

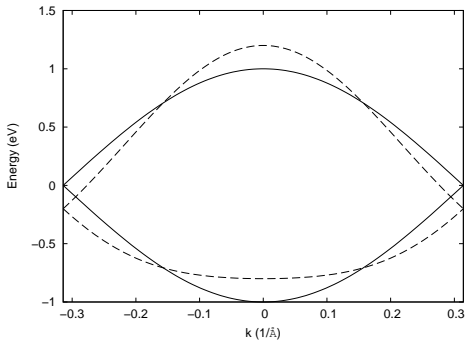[2]Of course we could retain γ terms from atoms further away and use the general result for H_{AA} from Eq. 24.

Figure 8: Example dispersion relation (Eq. (29)) for *trans*-polyacetylene, plotted within the first BZ. In this example $a = 10$ Å, $\epsilon_p = 0$ eV and $\gamma(|\boldsymbol{\tau}|) = 0.5$ eV. The solid lines show the band structure in a calculation with $\gamma(a) = 0$ eV, and the dashed lines show the 2 bands calculated with $\gamma(a) = 0.1$ eV. In both cases the band width is $4\gamma(|\boldsymbol{\tau}|) = 2$ eV.

3.8 Contributions from more than one orbital

In general, bands will contain contributions from more than one type of orbital. In graphene, for example, the lowest energy valence bands (which form the bonds between atoms) and the highest energy conduction bands, are constructed from a mixture of s, p_x and p_y orbitals (this is known as sp$_2$ hybridisation).

However, it is very easy to generalise the formalism in Eq.s (19) and (20) to deal with multiple types of orbital. All we need to do is use the index i to label both different basis sites *and* different orbital types.

For example, imagine a $N_b = 2$ basis crystal in which s, p_x, p_y and p_z orbitals all contribute to the bands of interest. We would then expect $2 \times 4 = 8$ bands (from $N_b = 2$ atoms per unit cell, with 4 orbitals per atom) and we would have to solve an 8×8 matrix eigenvalue equation to find the energies at each $\mathbf{k}$. In this case, if $i = 1$ labels an s-orbital on basis site A, and $j = 5$ labels a p_x orbital on basis site B the relevant hamiltonian matrix element would be,

$$H_{ij} = \frac{1}{N} \sum_{\mathbf{R}_A} \sum_{\mathbf{R}_B} e^{i\mathbf{k}\cdot(\mathbf{R}_A - \mathbf{R}_B)} \int \phi_s^*(\mathbf{r} - \mathbf{R}_A) H \phi_{p_x}(\mathbf{r} - \mathbf{R}_B) d\mathbf{r}. \qquad (30)$$

The rest of the hamiltonian matrix elements could be calculated in a similar way and then, as usual, the dispersion relation would be found by solving,

$$|\mathbf{H} - E(\mathbf{k})\mathbf{I}| = 0.$$

As an example of this type of calculation, Fig. 9 shows the dispersion relation for graphene calculated within an orthogonal tight binding scheme using 4 types of orbital: s, p_x, p_y and p_z. As graphene is a 2D hexagonal crystal with 2 atoms in the basis we get 8 bands in total.
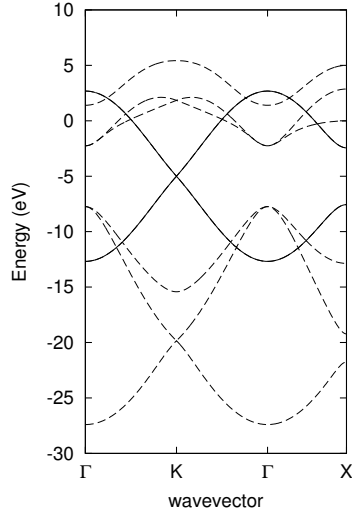
14

Figure 9: Calculated $E(\mathbf{k})$ for graphene using the overlap parameters of Popov *et al* Phys. Rev. B **70**, 115407 (2004). Graphene is a 2D crystal with a 2-atom basis in which s, p_x, p_y and p_z orbitals all contribute to the bands. The planar symmetry means we can separate the 8×8 matrix equation into 2 matrix equations: a 6×6, and a 2×2. The s, p_x and p_y orbitals mix to form 6 bands (shown in dashed lines). The p_z orbitals form the conduction and valence bands at the Fermi level (solid lines).

A Normalisation of LCAO wavefunction

If, from Eq. (6), our linear combination of atomic orbitals is

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r} - \mathbf{R}),$$

then the normalisation integral is,

$$
\begin{aligned}
I &= \int \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r} \\
&= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} \int e^{-i\mathbf{k}\cdot\mathbf{R}} \phi_n^*(\mathbf{r} - \mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}'} \phi_n(\mathbf{r} - \mathbf{R}') d\mathbf{r} \\
&= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \int \phi_n^*(\mathbf{r} - \mathbf{R}) \phi_n(\mathbf{r} - \mathbf{R}') d\mathbf{r},
\end{aligned}
$$

where each of the sums over $\mathbf{R}$ and $\mathbf{R}'$ go over the N possible translation vectors in the crystal.

However, from Eq. (4), $\int \phi_n^*(\mathbf{r}) \phi_n(\mathbf{r} - \mathbf{R}) d\mathbf{r} = \delta(\mathbf{R})$, where $\delta(\mathbf{R})$ is equal to one if $\mathbf{R} = 0$ and zero otherwise. Hence,

$$
\begin{aligned}
I &= \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \delta(\mathbf{R} - \mathbf{R}') \\
&= \frac{1}{N} \sum_{\mathbf{R}} \\
&= 1, \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (31)
\end{aligned}
$$

and the linear combination of atomic orbitals in Eq. (6) is correctly normalised.