Background to tight binding band structure of graphene

Introduction

The tight binding approach to electronic band structure is one of the standards of condensed matter physics and is frequently extended to the study of many body problems. The starting point is to assume a basis set of localized orbitals on each site of an atomic structure. The atomic structure does not have to be crystalline though often crystallinity is the correct assumption. The simplest model consists of assuming that only one localized orbital is important at each site, a so-called single band model. Some crystal structures, such as the honeycombe and fcc lattices, have more than one site per unit cell and require a slightly more complex treatment. In cases where there is periodicity, only one orbital per site and one orbital per unit cell, \( \phi \), Bloch’s theorem states that the wavefunction for an electron is,

\[
\psi_{k}(\vec{r}) = A_N \sum_{j} e^{i \vec{k} \cdot \vec{R}_j} \phi(\vec{r} - \vec{R}_j)
\]

If there are more orbitals per site and/or more than one atom per unit cell this expression is extended in a reasonably straightforward way. Here \( A_N \) is the normalization constant that is usually \( 1/N^{1/2} \). It falls out of the band energy calculations and is the band wavefunctions are normalized at the end, so sometimes it is omitted.

The tight binding method can also be used in cases where there is no lattice periodicity so that Bloch’s theorem fails. In this more general case the band structure problem requires solution of large sparse matrices. The general case considers a set of localized orbitals \( \phi_n \) and the assumption that the wavefunction of the system is a linear combination of atomic orbitals (LCAO),

\[
\psi(\vec{r}) = \sum_n c_n \phi_n(\vec{r})
\]

The orbitals \( \phi_n \) are call the basis set while \( c_n \) are the coefficients of the wavefunction that we would like to find. Notice that Bloch’s theorem is a special case of LCAO where the wavenumber \( \vec{k} \) is a good quantum number. Now we consider \( H \psi = E \psi \) which gives,

\[
\sum_n c_n(H - E)\phi_n = 0, \quad \text{so that} \quad \sum_n c_n(<m|H|n > -E <m|n>) = 0 = \sum_n (H_{mn} - ES_{mn})c_n
\]
where the Dirac notation $< m|O|n > = \int d^d\mathbf{r} \psi^*(\mathbf{r}) O \psi(\mathbf{r})$. The diagonal terms $< n|H|n > = \epsilon_n$ are the energies of the basis states, while the diagonal term $< n|n > = 1$ provided we use an orthonormal basis. In many cases, it is assumed that the overlap integrals $S_{m\neq n}$ are relatively small and can be ignored. This is NOT the case for graphene where they make an important contribution. In many cases the matrix elements $H_{mn}$ and $S_{mn}$ are found using either ab-initio methods or experimental data. The band structure is then found using the matrix equation to find the energy levels $E$ and wavefunction coefficients $c_n$.

As an example consider the tightbinding band structure of a set of hydrogen atoms that are separated by distance $a$ on a one dimensional chain with periodic boundary conditions. We consider local atomic 1s orbitals at each site. The one dimensional chain has only one atom per unit cell. We can then directly apply Bloch’s theorem (Eq. 1). In this problem the dominant terms are the nearest neighbor terms, so we only consider $H_{n,n-1} = t$ and $H_{n,n+1} = t$, $S_{n,n-1} = s$ and $S_{n,n+1} = s$ with all other off diagonal matrix elements set to zero. In that case the Hamiltonian matrix is tridiagonal and symmetric, with the diagonal elements equal to the energy of a 1s Hydrogen atom ($\epsilon = 13.6eV$). The lattice vectors are then $R_j = ja$, where $j$ is an integer. Bloch’s theorem then states that the coefficients $c_n = e^{-kna}$ where $k$ is an integer. Now if we plug this into the last of Eq. (), we find (for all $n$),

$$[e + t(e^{-ika} + e^{ika}) - E - sE(e^{-ika} + e^{ika})]e^{ika} = 0; \quad \text{so that} \quad E_k = \frac{e + 2t\cos(ka)}{1 + 2s\cos(ka)}$$

(4)

Because we want the wave function to be single valued, periodic boundary conditions imply that $e^{ik(N+1)a} = e^{ika}$, so that $k = 2\pi l / N$, with $l$ an integer. There is a different eigenvalue for each $k$ and a total of $N$ eigenvalues for an $N$ atom system.

Generalization of the approach above to Hypercubic lattices is straightforward. We just introduce analogous terms in the other directions, so that for example on a cubic lattice the bands are given by,

$$E_k = \frac{e + 2t(\cos(k_xa) + \cos(k_ya) + \cos(k_za))}{1 + 2s(\cos(k_xa) + \cos(k_ya) + \cos(k_za))}$$

(5)

Extension to the cases where there are more than one atom per unit cell or where more than one energy level per site is required lead to more interesting extensions. The case of graphene is where
there are two atoms per unit cell and only one orbital is considered, \( p_z \) that is the non-bonded orbital of the graphene system. The band structure of Silicon also has two atoms per unit cell and is quite challenging and there has been a great deal of study using ab-initio methods that usually grossly underestimate the band gap. A tight binding model that considers four orbitals per site with parameters taken from experiments does pretty well. In this case the band structure requires use of Bloch’s theorem to reduce the system to blocks of \( 8 \times 8 \) that are diagonalized numerically.

In the Anderson model the matrix is still taken to be tridiagonal in one dimension, moreover we assume that \( S_{m\neq n} = 0 \). The only complication is that the site energies \( \epsilon_i \) are drawn from a random distribution so Bloch’s theorem does not hold. We then have to find the eigenvalues and eigenvectors of a matrix that has dimensions \( N \times N \) where \( N \) is the number of atoms in the system. If we wanted to study the effect of disorder on the band structure of Graphene we would again consider the eigenvalues of an \( N \times N \) matrix, while for Si it would be \( 4N \times 4N \).

**Graphene**

Graphene has a planar structure where the chemical bonds are due to \( sp^2 \) orbitals. The remaining unbonded \( p \) orbital is by convention called the \( p_z \) orbital and it has \( \pi \) orientation with \( p_z \) orbitals of other carbon atoms in a graphene sheet. We only include the \( p_z \) orbital on each site in the tight binding calculation of the graphene band structure. The covalently bonded orbitals are much lower in energy and the 3s orbitals are much higher in energy so this is a reasonable approximation. Graphene has two sites in its unit cell, \( A \) and \( B \), as illustrated in Fig. 1 of Reich et al. These two sites in combination with the basis vectors

\[
\vec{a}_1 = \frac{\sqrt{3}}{2} \hat{x} + \frac{1}{2} \hat{y}; \quad \vec{a}_2 = \frac{\sqrt{3}}{2} \hat{x} - \frac{1}{2} \hat{y}
\]

(\( \vec{R}_j = n_1 \vec{a}_1 + n_2 \vec{a}_2 \)) enable reconstruction of the infinite graphene sheet.

If there are two atoms per unit cell (as for graphene) then Bloch’s theorem becomes,

\[
\psi_k(\vec{r}) = AN \sum_{\vec{R}_j} e^{i \vec{k} \cdot \vec{R}_j} \left[ a_k \phi^A_k(\vec{r} + \vec{\delta}_A - \vec{R}_j) + b_k \phi^B_k(\vec{r} + \vec{\delta}_B - \vec{R}_j) \right] = a_k \psi^A_k + b_k \psi^B_k
\]

where \( \vec{\delta}_A \) is the vector from the Bravais lattice point to atom A and \( \vec{\delta}_B \) is the vector from the Bravais lattice point to atom B. Multiplying on the left of this equation by the conjugate of \( \psi^A_k \) and
integrating gives,

\[(H_{AA} - E(k)S_{AA})a_k + (H_{AB} - E(k)S_{AB})b_k = 0.\] (8)

Similarly,

\[(H_{BA} - E(k)S_{BA})a_k + (H_{BB} - E(k)S_{BB})b_k = 0\] (9)

where \(H_{ij} = \langle \psi_i^k | H | \psi_j^k \rangle\) and \(S_{ij} = \langle \psi_i^k | \psi_j^k \rangle\) with \(i, j = A, B\). Also \(H_{BA} = H_{AB}^*, S_{BA} = S_{AB}^*\).

Writing these equations in matrix form and taking a determinant of the matrix yields Eq. (1) of Reich et al.