Tight Binding project

The project

This project can be carried out using any programming language and is perhaps easiest using Mathematica or Matlab. It has two parts.

1. Plot the band dispersion relations for electrons on square and hexagonal lattices (graphene). The objective is to show that for the square lattice the dispersion relations near the band extrema are parabolic. This is the usual behavior for almost all materials, e.g. Si, Ge etc. In constrast for Graphene the behavior near the extrema are linear, like in relativistic systems, which motivates a great deal of interest in studying the electronic properties of graphene. (details are given below)

2. Set up the nearest neighbor tight binding matrices for the square lattice with uniform random site energies (Anderson model). Diagonalize this matrix using canned routines (e.g. Eigenvalues in Mathematica). Plot the density of states and the participation ratio (see Eq. (11)) as a function of the disorder.

Background on tight binding for part 1

You can follow the paper S. Reich, J. Maultzsch, C. Thomsen, P. Ordejon, Phys. Rev. B66, 035412 (2002) for the graphene calculation. For the square lattice see equation (5) below.

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, ϕ, Bloch's theorem states that the wavefunction for an electron is,

$$\psi_{\vec{k}}(\vec{r}) = A_N \sum_n e^{i\vec{k}\cdot\vec{R}_n} \phi(\vec{r} - \vec{R}_n) = \sum_n c_n \phi_n(\vec{r}) \tag{1}$$

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 ϕ_n and the assumption that the wavefunction of the system is a linear combination of atomic orbitals (LCAO),

$$\psi(\vec{r}) = \sum_n c_n \phi_n(\vec{r}) \tag{2}$$

The orbitals ϕ_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,

$$\sum_n c_n (H - E)\phi_n = 0, \quad \text{so that} \quad \sum_n c_n (< m|H|n > -E < m|n >) = 0 = \sum_n (H_{mn} - ES_{mn}) c_n \tag{3}$$

where the Dirac notation $< m|O|n >= \int d^d r \psi^*(\vec{r}) O \psi(\vec{r})$. 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 intergrals $S_{m\neq n}$ 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),

$$[\epsilon + t(e^{-ika} + e^{ika}) - E - sE(e^{-ika} + e^{ika})]e^{ikna} = 0; \quad \text{so that} \quad E_k = \frac{\epsilon + 2tcos(ka)}{1 + 2scos(ka)} \tag{4}$$

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,

$$E_{\vec{k}} = \frac{\epsilon + 2t(cos(k_x a) + cos(k_y a) + cos(k_z a))}{1 + 2s(cos(k_x a) + cos(k_y a) + cos(k_z a))} \tag{5}$$

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 × 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 ϵ_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 orbit als. The remaining unbonded p orbital is by convention called the p_z orbital and it has π 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

$$\vec{a}_1 = \frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}; \quad \vec{a}_2 = \frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y} \tag{6}$$

($\vec{R}_j = n_1\vec{a}_1 + n_2\vec{a}_2$) enable reconstruction of the infinite graphene sheet. For a Bravais lattice we have $\vec{k} \cdot \vec{a} = 2\pi n$

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

$$\psi_{\vec{k}}(\vec{r}) = A_N \sum_{\vec{R}_j} e^{i\vec{k}\cdot\vec{R}_j}[a_{\vec{k}}\phi^A_{\vec{k}}(\vec{r} + \vec{\delta}_A - \vec{R}_j) + b_{\vec{k}}\phi^B_{\vec{k}}(\vec{r} + \vec{\delta}_B - \vec{R}_j)] = a_{\vec{k}}\psi^A_{\vec{k}} + b_{\vec{k}}\psi^B_{\vec{k}} \tag{7}$$

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 $\psi^A_{\vec{k}}$ and integrating gives,

$$(H_{AA} - E(k)S_{AA})a_{\vec{k}} + (H_{AB} - E(k)S_{AB})b_{\vec{k}} = 0. \tag{8}$$

Similarly,

$$(H_{BA} - E(k)S_{BA})a_{\vec{k}} + (H_{BB} - E(k)S_{BB})b_{\vec{k}} = 0 \tag{9}$$

where $H_{ij} =< \psi^i_{\vec{k}}|H|\psi^j_{\vec{k}} >$ and $S_{ij} =< \psi^i_{\vec{k}}|\psi^j_{\vec{k}} >$ 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. (some more details of the derivation are given in Appendix 1).

Tight binding and the Anderson model

Here we make a further approximation and ignore the term $< m|n >$ which is quite a rough approximation but can be reintroduced relatively easily later. Moreover the tight binding model is often written in second quantized form which is the usual form that is used in almost all theoretical papers on the many body problem (see Appendix 2 for background). The band problems we have studied may be written in the form,

$$H_{TB} = \sum_i \epsilon_i n_i + \sum_{ij} t_{ij} c_i^\dagger c_j \tag{10}$$

where t_{ij} is the overlap integral that we use in the calculation and the sum is over all neighbors considered in the calculation. Here we consider a one band model where there is only one orbital per site (like our models of Graphene above). In the simplest case, we only consider nearest neighbors. ϵ_i are the atomic energy levels at each site and in the graphene case ϵ is the energy of a p_z orbital. The band structure is found by setting up the tight binding matrix and diagonalizing it to find the energy levels in the band. We also get the band eigenfunctions or wavefunctions.

The Anderson model considers the effect of disorder on the wavefunctions. If there is disorder in ϵ_i it is the Anderson model, while if we consider disorder in the hopping elements t_{ij} it is called off-diagonal disorder. The key question is whether the wavefunctions become localized as a function of the disorder. To test this we calculate the participation ratio R for each eigenfunction defined as,

$$R = \frac{(\sum_i |\psi_i|^2)^2}{\sum_i |\psi_i| 4} \tag{11}$$

What behavior of R is expected for fully localized as opposed to fully extended states? Here ψ_i are the elements of the normalized wavefunction.

In this project you should set $t = 1$ and consider diagonal disorder where ϵ_i is drawn randomly from a distribution $[-W, W]$, where W is the width of the distribution. For wavefunctions near the band edge and band center, plot IPR as a function of W, for square lattices of different size.

Appendix 1 - More details on tight binding for graphene

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. We use that approximation for Graphene, where for a graphene sheet that lies in the x-y plane. Our localized orbitals are thus p_z orbitals on the sites of a honeycombe lattice.

The localized basis set is $\phi(\vec{r}-\vec{R}_j)$ where $\vec{R}_j$ is the location of the i^{th} atom of the honeycombe lattice and $\phi(\vec{r})$ is the p_z wavefunction. In its simplest form, and the one often used, the tight binding method is a single electron model where an the l^{th} electron is described by the Hamiltonian,

$$H_l = -\frac{\hbar^2}{2m}\nabla_l^2 + \sum_i V(\vec{r}_l - \vec{R}_j) \tag{12}$$

and the N-electron Hamiltonian is $\sum_l H_l$. In the tight binding method, H_l is broken into two parts

$$H_l = -\frac{\hbar^2}{2m}\nabla_l^2 + V(\vec{r}_l - \vec{R}_j) + \sum_{j\neq l} V(\vec{r}_l - \vec{R}_j) = H_l^0 + \delta V \tag{13}$$

where δV is treated as a perturbation - the eigenfunction of H_l^0 is $\phi(\vec{r}-\vec{R}_i)$.

A second key ingredient in that the wavefunction of the tight-binding Hamiltonian must obey Bloch's theorem (for a case with one atom per unit cell),

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}_j} e^{i\vec{k}\cdot\vec{R}_j}\phi(\vec{r}-\vec{R}_j) \tag{14}$$

Bloch's theorem reduces to the requirement that the above wavefunction must be an eigenstate of the translation operator $T_{\vec{R}_j} = exp[i\hat{p}\cdot\vec{R}_j/\hbar]$. In Mathematical terms this is just the observation that periodic systems are solved by a Fourier transform. The complexity here is that the Fourier transform must include the particular lattice structure that is present in the system. If there are two atoms per unit cell (as is the case for a honeycombe) then we have,

$$\psi_{\vec{k}}(\vec{r}) = a_{\vec{k}}\psi^A_{\vec{k}}(\vec{r}) + b_{\vec{k}}\psi^B_{\vec{k}}(\vec{r}) \tag{15}$$

where

$$\psi^\alpha_{\vec{k}}(\vec{r}) = \sum_{\vec{R}_j} e^{i\vec{k}\cdot\vec{R}_j}\phi^\alpha(\vec{r}+\vec{\delta}_\alpha-\vec{R}_j) \tag{16}$$

where α is A or B. With this assumption we then look for solutions to

$$H\psi_{\vec{k}} = \epsilon_{\vec{k}}\psi_{\vec{k}} \tag{17}$$

Multiplying on the left of this equation by $\psi^*_{\vec{k}}$ gives the matrix equation

$$\vec{v}^\dagger_{\vec{k}}\hat{H}_{\vec{k}}\vec{v}_{\vec{k}} = \epsilon_{\vec{k}}\vec{v}^\dagger_{\vec{k}}\hat{S}_{\vec{k}}\vec{v}_{\vec{k}} \tag{18}$$

where

$$\vec{v}^\dagger_{\vec{k}} = (a^*_{\vec{k}}, b^*_{\vec{k}}) \tag{19}$$

and the Hamiltonian Matrix is,

$$H_{\alpha,\beta} =< \psi^\alpha_{\vec{k}}(\vec{r})|H|\psi^\beta_{\vec{k}}(\vec{r}) > \tag{20}$$

while the overlap matrix is

$$S_{\alpha,\beta} =< \psi^\alpha_{\vec{k}}(\vec{r})|\psi^\beta_{\vec{k}}(\vec{r}) > \tag{21}$$

Note that often the latter overlap corrections are often neglected, however in graphene they are important and need to be kept.

The general expressions for H and S are

$$H^{\alpha\beta}_{\vec{k}} = \sum_{\vec{R}_m\vec{R}_l} e^{i\vec{k}\cdot(\vec{R}_l-\vec{R}_m)} < \phi^\alpha_{\vec{k}}(\vec{r}+\vec{\delta}_\alpha-\vec{R}_l)|H|\phi^\beta_{\vec{k}}(\vec{r}+\vec{\delta}_\beta-\vec{R}_k) > \tag{22}$$

Using translation invariance, this is,

$$H^{\alpha\beta}_{\vec{k}} = N\sum_{\vec{R}_l} e^{i\vec{k}\cdot\vec{R}_l} < \phi^\alpha_{\vec{k}}(\vec{r})|H^0+\delta V|\phi^\beta_{\vec{k}}(\vec{r}+\vec{\delta}_{\alpha\beta}-\vec{R}_l) >= N(\epsilon^\alpha s^{\alpha\beta}_{\vec{k}} + t^{\alpha\beta}_{\vec{k}}) \tag{23}$$

where $\vec{\delta}_{ij} = \vec{\delta}_j - \vec{\delta}_i$, and

$$s_{\vec{k}}^{\alpha\beta} = \sum_{\vec{R}_l} e^{i\vec{k}\cdot\vec{R}_l} < \phi_{\vec{k}}^{\alpha}(\vec{r} + \vec{\delta}_\alpha - \vec{R}_l)\phi_{\vec{k}}^{\beta}(\vec{r} + \vec{\delta}_\beta - \vec{R}_k) > \tag{24}$$

and

$$t_{\vec{k}}^{\alpha\beta} = \sum_{\vec{R}_l} e^{i\vec{k}\cdot\vec{R}_l} < \phi_{\vec{k}}^{\alpha}(\vec{r} + \vec{\delta}_\alpha - \vec{R}_l)|\delta V|\phi_{\vec{k}}^{\beta}(\vec{r} + \vec{\delta}_\beta - \vec{R}_k) > \tag{25}$$

In the case of Graphene the neighbor and next nearest neighbor hopping elements are,

$$t =< \phi^A * (\vec{r})|\delta V|\phi^B(\vec{r} + \vec{\delta}_3) >; \quad t_n nn =< \phi^A * (\vec{r})|\delta V|\phi^A(\vec{r} + \vec{a}_1) > \tag{26}$$

and

$$s =< \phi^A * (\vec{r})|\phi^B(\vec{r} + \vec{\delta}_3) > .$$

Appendix 2 : Second quantization

First quantization is the transition from the classical momentum to the quantum momentum, i.e. $p \to -i\hbar\nabla$. A many body Hamiltonian is written in terms of these operators, and we solve for a many body wavefunction that has a specific number of particles. In second quantization we allow the possibility of any number of particles, as we did in the ideal Fermi and Bose gases. Moreover we work in the "number representation" rather than working with the many body wavefunctions. Before going to the many particle case it may be useful to remember the use of raising an lowering operators in the Harmonic oscillator.

1. *Second quantization of a harmonic oscillator*

Creation and annihilation operators are the same as raising and lowering operators, and for a harmonic oscillator they are defined by,

$$a = \alpha(x + i\frac{p}{m\omega}); a^\dagger = \alpha(x - i\frac{p}{m\omega}); \quad \alpha = (\frac{m\omega}{2\hbar})^{1/2} \tag{27}$$

and

$$[a, a^\dagger] = 1; \quad [a, a] = [a^\dagger, a^\dagger] = 0; \tag{27}$$

and

$$\hat{n} = a^\dagger a; \quad \hat{n}|n >= n|n >; \quad H = (\hat{n} + \frac{1}{2})\hbar\omega \tag{27}$$

with

$$a^\dagger|n >= (n+1)^{1/2}|n+1 >; \quad a|n >= (n)^{1/2}|n-1 > . \tag{27}$$

2. *Second quantization of many-body Boson systems*

This formulation can be extended to treat a many body system composed of many harmonic oscillators that interact. In that case, if there are N harmonic oscillators, and the number representation of a state gives the number of bosons in each state, that is $|n_1, n_2 .... n_M >$ for a system with M single particle energy levels. The creation and annihilation operators obey the relations,

$$[a_i, a_j^\dagger] = \delta_{ij}; \quad [a_i, a_j] = 0; \quad [a_i^\dagger, a_j^\dagger] = 0 \tag{27}$$

and,

$$\hat{n}_i = a_i^\dagger a_i; \quad \hat{n}_i|n_1 ... n_i + 1 ... n_M >= n_i|n_1 ... n_i + 1 ... n_M >; \tag{27}$$

and

$$a_i^\dagger|n_1 ... n_i ... n_m >= (n_i + 1)^{1/2}|n_1 ... n_i + 1 ... n_M >; \tag{27}$$

$$a_i|n_1 ... n_i ... n_M >= (n_i)^{1/2}|n_1 ... n_i - 1 ... n_M > \tag{27}$$

These operators act in the state space of many body wavefunctions constructed from single particle states, for example for a set of Harmonic oscillators, we need to construct a correctly symmetrized N harmonic oscillator wavefunction basis set. A state of this type is written in second quantized form as,

$$|n_1....n_i...n_M >= (a_M^\dagger)^{n_M}..(a_i^\dagger)^{n_i}...(a_1^\dagger)^{n_1}|0> \tag{27}$$

In field theory, the interactions are often written in real space where they are called field operators. Creation and annihilation then occurs at a point in space. Nevertheless Boson second quantized field operators obey the similar commutation relations,

$$[\psi(x),\psi^\dagger(x')] = \delta(x-x'); \quad [\psi(x),\psi(x')] = [\psi(x)^\dagger,\psi^\dagger(x')] = 0; \quad \hat{n}(x) = \psi(x)^\dagger\psi(x) \tag{27}$$

3. *Second quantization of many-body Fermion systems*

In the case of Fermions, there are two differences: (i) each state can only have one or zero particles, (ii) the commutators change to anticommutators, so that,

$$\{a_i, a_j^\dagger\} = \delta_{ij}; \quad \{a_i, a_j\} = 0; \quad \{a_i^\dagger, a_j^\dagger\} = 0 \tag{27}$$

and,

$$\hat{n}_i = a_i^\dagger a_i; \quad \hat{n}_i|n_1...n_i+1...n_M >= n_i|n_1...n_i+1...n_M >; \tag{27}$$

and

$$a_i^\dagger|n_1...n_i...n_m >= (-1)^{S_k}\delta(n_i)|n_1...n_i+1...n_M >; \tag{27}$$

and

$$a_i|n_1...n_i...n_M >= (-1)^{S_k}\delta(n_i-1)|n_1...n_i-1...n_M > \tag{27}$$

where $S_k = \sum_{j=1}^{i-1} n_j$. These operators act in the state space of many body wavefunctions constructed from single particle states. In the case of Fermions, the correct wave functions are Slater determinants, which have the form,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}. \tag{27}$$

A state of this type is written in second quantized form as,

$$|n_1....n_i...n_M >= (a_M^\dagger)^{n_M}..(a_i^\dagger)^{n_i}...(a_1^\dagger)^{n_1}|0> \tag{27}$$

In field theory, Fermion second quantized field operators obey the commutation relations,

$$\{\psi(x), \psi^\dagger(x')\} = \delta(x - x'); \quad \{\psi(x), \psi(x')\} = \{\psi(x)^\dagger, \psi^\dagger(x')\} = 0; \quad \hat{n}(x) = \psi(x)^\dagger \psi(x) \tag{27}$$

4. *Hamiltonians in second quantized form, both Bosons and Fermions*

To work with these operators, we need to write the quantum Hamilonians that we are interested in second quantized form. This is relatively straightforward, as we can write a single particle wavefunction as,

$$\psi(\vec{r}) = \sum_k \psi_k(\vec{r}) a_k^\dagger |0> \tag{27}$$

so the second quantized form for the kinetic energy may be written as,

$$\hat{O} = \sum_{k_1,k_2} a_{k_1} O_{k_1,k_2} a_{k_2}^\dagger, \quad O_{k_1,k_2} = \int d^3r \psi_{k_1}^*(\vec{r}) O(\vec{r}) \psi_{k_2}(\vec{r}) \tag{27}$$

and for a pair potential we have,

$$\hat{V} = \sum_{k_1,k_2,k_3,k_4} a_{k_1}^\dagger a_{k_2}^\dagger V_{k_1,k_2,k_3,k_4} a_{k_3} a_{k_3}, \quad V_{k_1,k_2,k_3,k_4} = \int d^3r d^3r' \psi_{k_1}^*(\vec{r}) \psi_{k_2}^*(\vec{r}') V(\vec{r}, \vec{r}') \psi_{k_3}(\vec{r}) \psi_{k_4}(\vec{r}') \tag{27}$$

Note that the order of the operators must be with the destruction operators to the right so the vacuum state has zero energy. This form of the Hamiltonian applies to both Fermions and Bosons, as the commutation (Bosons) and anticommutation (Fermion) relations account for the symmetry of the particles.