Chapter 1

Periodic systems and the Bloch Theorem

1.1 Introduction

We are interested in solving for the eigenvalues and eigenfunctions of the Hamiltonian of a crystal. This is a one-electron Hamiltonian which has the periodicity of the lattice.

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\boldsymbol{r}). \tag{1.1}$$

If $\mathbf{R}$ is a translation vector of the lattice, then $V(\boldsymbol{r}) = V(\boldsymbol{r} + \mathbf{R})$. To solve for such a problem, one must first consider the boundary conditions that the eigenfunctions must satisfy. In a crystal, we require them to be periodic of period $N_i\mathbf{R}_i$; $(i = 1, 2, 3)$ for large N_i. Typically, N_i is of the order of the size of the crystal: $N_1N_2N_3 \simeq 10^{23}$! A good basis to describe such functions are plane waves $\exp\,(i\mathbf{k}.\boldsymbol{r})$. Applying the boundary conditions to the plane waves implies that the momenta $\mathbf{k}$ must be discrete points: $k_i = 2\pi n_i/N_iR_i$; $i = 1, 2, 3$ where n_i are integers. Practically, for large N_i, they form a continuous set of points in the reciprocal space. In the following, we will first introduce and prove Bloch's theorem which is based on the translational invariance of the system; then make use of it to simplify the difficult task of finding the eigenstates and eigenvalues of the infinite crystal Hamiltonian.

1.2 Bloch Theorem

Let $T_{\mathbf{R}}$ be the translation operator of vector $\mathbf{R}$. $T_{\mathbf{R}}$ commutes with the Hamiltonian. Indeed, the kinetic energy is translationally invariant, and the potential energy is periodic:

$$[T_{\mathbf{R}}, V]f(\boldsymbol{r}) = T_{\mathbf{R}}V(\boldsymbol{r})f(\boldsymbol{r}) - V(\boldsymbol{r})T_{\mathbf{R}}f(\boldsymbol{r}) = V(\boldsymbol{r}+\mathbf{R})f(\boldsymbol{r}+\mathbf{R}) - V(\boldsymbol{r})f(\boldsymbol{r}+\mathbf{R}) = 0 \tag{1.2}$$

On the other hand, $[T_{\mathbf{R}}, T_{\mathbf{R}'}] = 0$. Thus, the Hamiltonian and all the translation operators of the crystal commute with each other. They possess, therefore, a common set of eigenstates.

Let us search then the eigenstates of the translation operators $T_{\mathbf{R}}$. For a general function satisfying the boundary conditions of the problem, one can write, after expanding the eigenstate on a plane wave basis, the eigenvalue equation as follows:

$$T_{\mathbf{R}}f(\boldsymbol{r}) = T_{\mathbf{R}}\sum_{\boldsymbol{q}} C_{\boldsymbol{q}}\, e^{i\mathbf{q}.\mathbf{r}} = \sum_{\boldsymbol{q}} C_{\boldsymbol{q}}\, e^{i\mathbf{q}.\mathbf{r}} e^{i\mathbf{q}.\mathbf{R}} = t_R \sum_{\boldsymbol{q}} C_{\boldsymbol{q}}\, e^{i\mathbf{q}.\mathbf{r}} \tag{1.3}$$

where we denoted the eigenvalue by t_R. In order for the above equality to be true, $e^{i\mathbf{q}.\mathbf{R}}$ must be a constant: $\mathbf{q}.\mathbf{R} = 2\pi n + \text{constant} \Rightarrow \mathbf{q} = \mathbf{k} + \mathbf{G}$ where $\mathbf{k}$ is an arbitrary vector and $\mathbf{G}$ is a **reciprocal lattice vector**: $\mathbf{G}.\mathbf{R} = 2\pi n$. The eigenvalue is therefore $t_R = e^{i\mathbf{k}.\mathbf{R}}$ and the eigenvector could be any plane wave of momentum $\mathbf{k} + \mathbf{G}$. The eigenvalue t_R being degenerate with respect to $\mathbf{k} + \mathbf{G}$, a general eigenvector associated with this eigenvalue can be written as:

$$f_{\mathbf{k}}(r) = \sum_{G} C_{\mathbf{k}+\mathbf{G}}\, e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}} = e^{i\mathbf{k}.\mathbf{r}} \sum_{G} C_{\mathbf{k}+\mathbf{G}}\, e^{i\mathbf{G}.\mathbf{r}} = e^{i\mathbf{k}.\mathbf{r}} u_{\mathbf{k}}(r) \tag{1.4}$$

The arbitrary vector $\mathbf{k}$ labels thus different eigenvalues and eigenstates of translation operators. Furthermore, the above function is also eigenstate of all possible translation operators of the lattice. Note that the infinite sum over all possible momenta $\boldsymbol{q}$ is now reduced to a discrete (still infinite) sum over the reciprocal lattice vectors, and that is a great simplification in the problem. We can also notice that all states corresponding to $\mathbf{k}$ and any $\mathbf{k} + \mathbf{G}$ are equal, i.e. the function $f_{\mathbf{k}}$ is periodic in the reciprocal space $f_{\mathbf{k}} = f_{\mathbf{k}+\mathbf{G}}, \forall \mathbf{G}$. Due to the previously-mentioned commutation relation, $f_{\mathbf{k}}$ is also eigenstate of $\mathcal{H}$. To obtain its coefficients $C_{\mathbf{k}+\mathbf{G}}$, we just need to insert this wavefunction into the Schroedinger equation. The Hamiltonian matrix must therefore be diagonalized in the space of all plane waves of momentum $\mathbf{k}+\mathbf{G}$ for any vector $\mathbf{k}$ chosen in the first Brillouin zone. Indeed the periodicity of $f_{\mathbf{k}}$ in the reciprocal space implies that it is sufficient to chose the arbitrary vector $\mathbf{k}$ in the first Brillouin zone.

Let us finally state **Bloch's theorem**: The eigenstates $f_{\mathbf{k}}$ of a periodic Hamiltonian can be written as a product of a periodic function with a plane wave of momentum $\mathbf{k}$ restricted to be in the first Brillouin zone $f_{\mathbf{k}}(\boldsymbol{r}) = u_{\mathbf{k}}(\boldsymbol{r})e^{i\mathbf{k}.\mathbf{r}}$ (with $u_{\mathbf{k}}$ periodic in $\mathbf{k}$ and in $\boldsymbol{r}$) ; furthermore $f_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}.\mathbf{R}} f_{\mathbf{k}}(\mathbf{r})$.

• Solution of the eigenvalue problem in general

The Schroedinger equation or the eigenvalue problem is written in the following form: $H\psi = E\psi$. Different Boundary Conditions (BC) apply for ψ of a crystal and a cluster. The basis set must therefore satisfy the same boundary conditions. This means that for an infinite crystal, the basis must satisfy periodic BCs, whereas for a molecule or a cluster, basis functions must go to zero at infinity. Let $\phi_i(\mathbf{r})_{i=1,\dots,N}$ be a *finite* basis set (hence incomplete description), and let us expand the eigenfunction ψ on this basis: $\psi(\mathbf{r}) = \sum_{i=1}^{N} C_i \phi_i(\mathbf{r})$. We have already seen that minimizing the expectation value of the Hamiltonian with the constraint of orthonormality (the variational formulation) is equivalent to inserting the expansion of the wavefunction into the Schroedinger equation and projecting it onto each of the basis functions. Both lead to the following set of linear equations:

$$\sum_{j=1}^{N} [H_{ij} - ES_{ij}]\, C_j = 0; \quad \forall i = 1, ..., N \tag{1.5}$$

where $H_{ij} = \int \phi_i^*(\mathbf{r})\, H\, \phi_j(\mathbf{r})\, d\mathbf{r}$ and $S_{ij} = \int \phi_i^*(\mathbf{r})\, \phi_j(\mathbf{r})\, d\mathbf{r}$ are the Hamiltonian an overlap matrix elements respectively.

• Solution of the Schroedinger equation in a periodic box

$$[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The “crystal potential” $V(\mathbf{r})$ is a periodic function: $V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r})$

We will therefore make use of the Fourier decomposition to describe it as:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} \hat{V}_{\mathbf{G}}\, e^{i\mathbf{G}\cdot\mathbf{r}}$$

where $\hat{V}_{\mathbf{G}} = \int_{cell} V(\mathbf{r})\, e^{-i\mathbf{G}\cdot\mathbf{r}}\, d\mathbf{r}/\Omega$; $\mathbf{G}$'s are reciprocal lattice vectors defined by $\mathbf{G}\cdot\mathbf{R} = 2n\pi$, $\mathbf{R}$'s are translation vectors of the crystal lattice and Ω is the unit cell volume. If $\{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3\}$ is the basis of the primitive cell, then the reciprocal lattice vectors are defined by:
$\mathbf{G}_i \cdot \mathbf{R}_j = 2\pi\delta_{ij}$, or more explicitly: $\mathbf{G}_1 = 2\pi(\mathbf{R}_2 \times \mathbf{R}_3)/\Omega$ with $\Omega = \mathbf{R}_1 \cdot (\mathbf{R}_2 \times \mathbf{R}_3)$ and so on ... We see that the $\mathbf{G}$'s appear naturally because of the periodicity of the potential.

The BC's satisfied by the wavefunctions come from Bloch's theorem:
For every eigenfunction ψ*, there exists a vector* $\mathbf{k}$ *such that* : $\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r})$; *in other words* $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$ *where* $u_{\mathbf{k}}$ *is a periodic function.* We see therefore that ψ is not periodic! To solve the eigenvalue problem, one may take any basis set satisfying the above theorem.

Plane wave method:

One simple and easy choice would be the plane waves: $\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{\Omega}$ which are eigenstates when $V(\mathbf{r}) = 0$. The eigenvalue equation in this basis may be written as:

$$\sum_{\boldsymbol{q}} [H_{\mathbf{k}\boldsymbol{q}} - E\, S_{\mathbf{k}\boldsymbol{q}}]\, C_{\boldsymbol{q}} = 0; \quad \forall\mathbf{k}$$

But $S_{\mathbf{k}\boldsymbol{q}} = \delta_{\mathbf{k},\boldsymbol{q}}$ and $H_{\mathbf{k}\boldsymbol{q}} = \delta_{\mathbf{k},\boldsymbol{q}}\, k^2/2m + \hat{V}_{\mathbf{k}-\boldsymbol{q}}$. Therefore, $\mathbf{k} - \boldsymbol{q} = \mathbf{G}$ must be a reciprocal lattice vector. So the overlap S is the identity and the Hamiltonian H couples any arbitrary vector $\mathbf{k}$ only to some $\mathbf{k}+\mathbf{G}$. The problem of having to diagonalize an “infinite” matrix H has been highly simplified to the diagonalization of many smaller matrices (one for each $\mathbf{k}$) of finite dimension (defined by the number of $\mathbf{G}$'s included in the Fourier expansion of $\mathbf{G}$). The final solutions for each $\mathbf{k}$ are therefore (this is another statement of Bloch's theorem):

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}}\; e^{i\mathbf{k}+\mathbf{G}\cdot\mathbf{r}}/\sqrt{\Omega}$$

for a Hamiltonian $H_{\mathbf{k}+\mathbf{G},\,\mathbf{k}+\mathbf{G}'} = H_{\mathbf{G}\mathbf{G}'}(\mathbf{k}) = \delta_{\mathbf{G}\mathbf{G}'}\,(\mathbf{k}+\mathbf{G})^2/2m + \hat{V}_{\mathbf{G}-\mathbf{G}'}$. Note that $\psi_{\mathbf{k}}$ has the additional property of being periodic in the reciprocal space: $\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$.

The number of obtained eigenvalues is equal to the number of chosen basis functions. The eigenvalues and eigenstates for each $\mathbf{k}$ will also be labeled by an integer λ which is called the band index ($\lambda = 1$ corresponds to the first band, $\lambda = 2$ represents the second band and so on...). Hence, the eigenfunctions and eigenvalues will be denoted respectively by $\psi_{\lambda\mathbf{k}}$ and $E_{\lambda\mathbf{k}}$.

The form of the Schroedinger's equation in the plane-wave basis is:

$$\left((\mathbf{k}+\mathbf{G})^2/2m + \hat{V}_0 - E_{\mathbf{k}+\mathbf{G}}\right) C_{\mathbf{k}+\mathbf{G}} + \sum_{\mathbf{G}'\neq\mathbf{G}} \hat{V}_{\mathbf{G}-\mathbf{G}'} C_{\mathbf{k}+\mathbf{G}'} = 0 \qquad (1.6)$$

or in terms of different bands λ (corresponding to different $\mathbf{G}$ vectors) [1].

$$\left((\mathbf{k}+\mathbf{G})^2/2m + \hat{V}_0 - E_{\mathbf{k},\lambda}\right) C^{\lambda}_{\mathbf{k}+\mathbf{G}} + \sum_{\mathbf{G}'\neq\mathbf{G}} \hat{V}_{\mathbf{G}-\mathbf{G}'} C^{\lambda}_{\mathbf{k}+\mathbf{G}'} = 0 \qquad (1.7)$$

In a plane wave calculation, the Fourier expansion has to be truncated at some $\mathbf{G}_{max}$ corresponding to a cutoff energy of $E_{\text{cutoff}} = \hbar^2\mathbf{G}^2_{max}/2m$. This basically defines the smallest wavelength one uses to describe the potential and the charge density. It only depends on the nature of the elements one is treating and not on the unit-cell size. However, the number of plane waves ($\mathbf{G}$'s) used in a calculation relate the two through: $N_{PW} \simeq G^3_{max}\Omega \simeq E^{3/2}_{\text{cutoff}}\Omega$. The cutoff energy should be chosen such that the total energy of the system has converged as a function of the latter. To achieve such convergence, rather high cutoff energies are required. In practice, however, usually differences in total energies are of interest. In this case, smaller cutoffs will be sufficient since systematic errors due to lack of convergence will cancel each other out.

Periodicity, broken symmetry and gap openings:

The effect ofperiodicity on the band structure can be investigated by solving exactly solvable models such as the Kroenig-Penney model in one dimension [2] Here, however, we will use the perturbation approach, where analytical formulas are available for the eigenstates and eigenvalues. Assuming the potential is weak, one can expand the eigenvalues and eigenstates in powers of

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[1] In the absence of a periodic potential, there is a one to one correspondance between a band labeled by λ and a reciprocal lattice vector $\mathbf{G}$, so that $E_{\mathbf{k},\lambda} = E_{\mathbf{k}+\mathbf{G}}$ and $C^{\lambda}_{\mathbf{k}+\mathbf{G}} = 1$ and $C^{\lambda}_{\mathbf{k}+\mathbf{G}'} = 0$ for all other $\mathbf{G}'$. In the presence of a weak periodic potential, a perturbative argument shows that these coefficients slightly vary from 1 and 0

[2] the potential is either that of a superlattice i.e. constant with different values in 2 chosen intervals, the sum of which is the period of the lattice; or it can be a "comb" function (sum of Dirac delta functions).

the potential.To first order in the eigenstates and second order in eigenvalues we have:

$$\psi_{\lambda \mathbf{k}} = e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}} + \sum_{\mathbf{G}' \neq \mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}').\mathbf{r}} \frac{\hat{V}_{\mathbf{G}-\mathbf{G}'}}{E_{\mathbf{k}+\mathbf{G}} - E_{\mathbf{k}+\mathbf{G}'}} \tag{1.8}$$

$$E_{\lambda \mathbf{k}} = \frac{(\mathbf{k}+\mathbf{G})^2}{2m} + \hat{V}_0 + \sum_{\mathbf{G}' \neq \mathbf{G}} \frac{|\hat{V}_{\mathbf{G}-\mathbf{G}'}|^2}{E_{\mathbf{k}+\mathbf{G}} - E_{\mathbf{k}+\mathbf{G}'}} \tag{1.9}$$

this expansion is valid whenever $\hat{V}_{\mathbf{G}-\mathbf{G}'} \ll |E_{\mathbf{k}+\mathbf{G}} - E_{\mathbf{k}+\mathbf{G}'}|$. We can therefore note that near the zone boundaries, where there is degeneragy, the denominator can become zero, and the expansion breaks down. In this case, one will keep in the expansion only the terms that have small denominator, the contribution of others being small in the $\hat{V} \to 0$ limit, as they are in $\hat{V}^2$. The divergence in the denominators happens for the **Bragg condition** $E_{\mathbf{k}+\mathbf{G}} = E_{\mathbf{k}+\mathbf{G}'}$ implying either $\mathbf{k} = 0$ and $|\mathbf{G}| = |\mathbf{G}'|$, or, $\mathbf{k} = \mathbf{G}_1/2$ and $\mathbf{G} = 0; \mathbf{G}' = -\mathbf{G}_1$ where $\mathbf{G}_1$ is the smallest vector of the reciprocal lattice. Here, for simplicity, we will restrict ourselves to the one-dimensional case where we only have two-fold degeneracies and diagonalizations can be done analytically. The Hamiltonian matrix in the case where there is only two-fold degeneragy (or near degeneracy) is:

$$\begin{bmatrix} E_{\mathbf{k}+\mathbf{G}} & \hat{V}_{\mathbf{G}-\mathbf{G}'} \\ \hat{V}^*_{\mathbf{G}-\mathbf{G}'} & E_{\mathbf{k}+\mathbf{G}'} \end{bmatrix} => \varepsilon_{\pm} = \frac{E_{\mathbf{k}+\mathbf{G}} + E_{\mathbf{k}+\mathbf{G}'}}{2} \pm \sqrt{\Delta^2 + |\hat{V}_{\mathbf{G}-\mathbf{G}'}|^2}$$

with $\Delta = (E_{\mathbf{k}+\mathbf{G}} - E_{\mathbf{k}+\mathbf{G}'})/2$. At the exact Bragg condition where $\Delta = 0$, we have splitting of the two eigenvalues by the perturbation: $\varepsilon_{\pm} = E_{\mathbf{k}+\mathbf{G}} \pm |\hat{V}_{\mathbf{G}-\mathbf{G}'}|$. So, the two degenerate bands become separated by a gap given by $2|\hat{V}_{\mathbf{G}-\mathbf{G}'}|$. As we previously said, this can happen at the zone center or boundary where the group velocity $\nabla_{\mathbf{k}} E$ is also equal to zero. The eigenstates are then either the sum or the difference of the two plane waves$\psi_{\pm} = e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}} \pm e^{i(\mathbf{k}+\mathbf{G}').\mathbf{r}}$ which are reduced to a sin and cos function. Near the zone boundary, however, where there is near degenearcy, the term Δ is small but nonzero. Qualitatively, the level repulsion still persists and the gap is even larger than at the zone boundary. It can be verified that the eigenstates become the product of the sin or cos functions times an envelope function of large wavelength. This wavelength being the inverse of the distance of the actual wavenumber from the zone boundary $\delta = \mathbf{k} - \mathbf{G}_1/2$.

Note that for the higher bands, the difference of the $\mathbf{G}$ vectors becomes larger, and since usually $\hat{V}_{\mathbf{G}}$ is a decreasing function of $\mathbf{G}$, the gaps become increasingly small for higher energy bands. The difference between a metal and a semiconductor is in the position of the Fermi level. If the latter lies within a band, one is dealing with a metal, and if it is in the gap (fully filled bands), one is dealing with a semiconductor.

Tight-binding or LCAO method:
In cases where some electronic states are very localized, it would take a large number of plane waves to describe them. Examples are core electrons in all-electron calculations, and d and f orbitals in transition metals and heavy atoms. In this case, one might prefer to expand the wavefunctions on localized, atomic-like basis functions. This method is called Tight-Binding (TB) or LCAO (standing for Linear Combination of Atomic Orbitals). Sometimes, TB also refers to semi-empirical methods in which the hopping matrix elements between neighboring atoms are determined from a fit to ab-initio or experimental data. Such a choice of basis also exists in mixed-basis methods, where the basis consists of both plane waves, to describe extended elecron states, and atomic-like orbitals to describe localized electron states. In a periodic system, the proper form of the basis functions satisfying Bloch's theorem should be:

$$\phi_{\mathbf{k}}^{\tau\alpha}(\mathbf{r}) = \sum_{\mathbf{R}} b_\alpha(\mathbf{r} - \mathbf{R} - \tau)\, e^{i\mathbf{k}\cdot\mathbf{R}}/\sqrt{N}$$

where the function $b_\alpha(\mathbf{r} - R - \tau)$ is an atomic-like orbital localized on the atomic position labeled τ within the unit cell defined by $\mathbf{R}$, and α is the orbital index $(s, p_x, p_y, p_z...)$.

Note that this expression is manifestly **G**-periodic (i.e. periodic in the reciprocal space). This change of basis from $(\mathbf{R}, \tau, \alpha)$ representation to the **Bloch basis**: $(\mathbf{k}, \tau, \alpha)$ is just a unitary transformation which makes use of the Bloch theorem ($\phi_{\mathbf{k}}^{\tau\alpha}(\mathbf{r} + \mathbf{R}) = \phi_{\mathbf{k}}^{\tau\alpha}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{R}}$) to make the matrix of Hamiltonian, as we will show below, block-diagonal, meaning that:

$$< \phi_{\mathbf{k}}^{\tau\alpha}|H|\phi_{\mathbf{k}'}^{\tau'\alpha'} > \propto \delta_{\mathbf{k},\mathbf{k}'+\mathbf{G}}$$

which is a great simplification of the diagonalization problem. The size of each bloch for a sampling k-point in the FBZ, is equal to the total number of orbitals present in the unit cell: ($\sum_{\tau\alpha} 1$=size of the Hamiltonian matrix in the Bloch basis).

$$\begin{aligned} < \phi^{\tau\alpha}_{\mathbf{k}}|H|\phi^{\tau'\alpha'}_{\mathbf{k}'} > &= \sum_{\mathbf{R}\mathbf{R}'} \frac{1}{N}\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, e^{i\mathbf{k}'\cdot\mathbf{R}'} \; < b_\alpha(\mathbf{r}-\mathbf{R}-\tau)|H|b_{\alpha'}(\mathbf{r}-\mathbf{R}'-\tau') > \\ &= \sum_{\mathbf{R}\mathbf{R}'} \frac{1}{N}\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, e^{i\mathbf{k}'\cdot\mathbf{R}'}\, f_{\tau\alpha,\tau'\alpha'}(\mathbf{R}-\mathbf{R}') \\ &= \sum_{\mathbf{R}} \frac{1}{N}\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \sum_{\mathbf{R}''} e^{-i\mathbf{k}'\cdot\mathbf{R}''}\, f_{\tau\alpha,\tau'\alpha'}(\mathbf{R}'') \\ &= \delta_{\mathbf{k},\mathbf{k}'+\mathbf{G}}\, [\sum_{\mathbf{R}''} e^{-i\mathbf{k}'\cdot\mathbf{R}''}\, f_{\tau\alpha,\tau'\alpha'}(\mathbf{R}'')] \qquad (1.10) \end{aligned}$$

showing the decoupling of different **k** vectors within the first Brillouin zone. Use of translational symmetry was made going from the first to the second line.

Note that the sum over $\mathbf{R}''$ involves only a small number of terms for which the hopping integrals $f_{\tau\alpha,\tau'\alpha'}(\mathbf{R}'')$ are nonzero. A similar expression holds for the overlap matrix, and one can, for each chosen k-point in the first Brillouin zone, solve the generalized eigenvalue problem with a matrix of size much smaller than in the plane wave method.

As will be shown in the exercises on the linear chain, the bandwidth wihin the TB formalism is proportional to the hopping integrals, and N-fold degenerate atomic levels fan into a continuum of width $4t$ as the interatomic distance becomes smaller and the hopping integral gets larger.

Figure 1.1: Energy levels of the system as at the atoms get closer to each other, and the hopping integral increases. The bandwidth essentially scales with the latter.

First Brillouin Zone and general considerations:

The LCAO Hamiltonian for **k** and any $\mathbf{k}+\mathbf{G}$ however, has the same matrix elements. This is similar to the plane wave method, where both the Hamiltonian and its eigenstates were shown to be periodic in **k**. Due to this periodicity in the reciprocal space, there is no need to treat all **k**'s; one only needs to treat the **k**'s inside the **First Brillouin Zone** (FBZ) which is the Wigner-Seitz cell of the reciprocal space. In practice, for numerical calculations, involving integrations over the **k**-points in the FBZ, one has to choose a grid of **k**-points. Because of the symmetries of the cell, if any, one needs to consider only the **k**-points in some portion of the FBZ. Furthermore, some *special* **k***-points* may be used to increase the computational efficiency. For more details about this topic, one may refer to the following papers:

- M. J. Mehl, *et al.*, Phys. Rev. B 41, 10311 (1990);
- H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
  or consult the following homepage to download **k**-point sets:
  http://dave.nrl.navy.mil/bind/kpts/index.html

Using the power of Bloch's theorem, one has been able to reduce the problem of diagonalizing an "infinite" Hamiltonian matrix, to diagonalizing a finite matrix (treating the atoms of the unit cell only) but for all the **k**-points in the FBZ. For metals or systems without a gap, the mesh should be a fine one, but for semi-conductors or insulators where the gap is non-zero, one may take a coarser **k**-point mesh. In any case, checks must be performed to make sure of the convergence of the results as a function of the number of k-points taken in the FBZ.

• Band Structure and Density Of States (DOS)

In an electronic structure calculation based on the density-functional or Hartree-Fock theory, once the self-consistency iterations have converged, one obtains the ground state charge density and the crystal potential. Using the eigenvalues at the k-points taken in the FBZ, one may also extract the density of states (DOS). After this calculation, one may also obtain the band structure curves by chosing another set of k-points taken along the symmetry directions in the FBZ, and calculating the eigenvalues for these k-points by using the converged and self-consistent charge density and crystal potential.

The DOS is defined (including the spin degeneracy) as

$$DOS(E) = 2 \sum_{\lambda \mathbf{k}} w_{\mathbf{k}} \delta(E - E_{\lambda \mathbf{k}})$$

If a fine k-grid is chosen, one can replace the delta function by a broadened Gaussian and perform the sum numerically. The broadening must be large enough or k-grid fine enough so that the delta contribution of each grid point does not appear as a spike in the DOS; and it should not be too large as to wash out the finer details of the DOS curve. The weighting factor $w_{\mathbf{k}}$ are there first to assure proper normalization[3] The best method for calculating the crystal DOS, is the tetrahedron method. In this method, one has calculated the eigenvalues at some k-points in the FBZ. It is possible to connect the k-points nearest to each other to obtain small tetrahedra (in 3D) or triangles (in 2D). One then assumes for each band a linear $E(k)$ in this region, and integrates over the tetrahedron volume analytically:

$$DOS(E) \propto \sum_{\lambda} \int \frac{dS_{\lambda\mathbf{k}}}{|\nabla_k E_{\lambda\mathbf{k}}|}$$

For the integration over the full volume of the FBZ, one also needs the energy eigenvalues at the zone boundaries and symmetry directions. These special points would come into the calculation with a different weight. Likewise, the band energy and the ground state charge density are a weighted sum of the eigenvalues and square of the eigenvectors respectively, over the FBZ:

$$E_{band} = \sum_{\lambda\mathbf{k}} w_{\mathbf{k}}\, E_{\lambda\mathbf{k}}\,; \quad \rho(r) = \sum_{\lambda\mathbf{k}}^{\text{occupied}} w_{\mathbf{k}}\, |\psi_{\lambda\mathbf{k}}(r)|^2$$

E_{band} is the total energy for a **non interacting** system. If interactions are present, even within a mean-field theory, a double counting correction term must be subtracted from this energy.
The general flowchart of a band structure calculation is described below:

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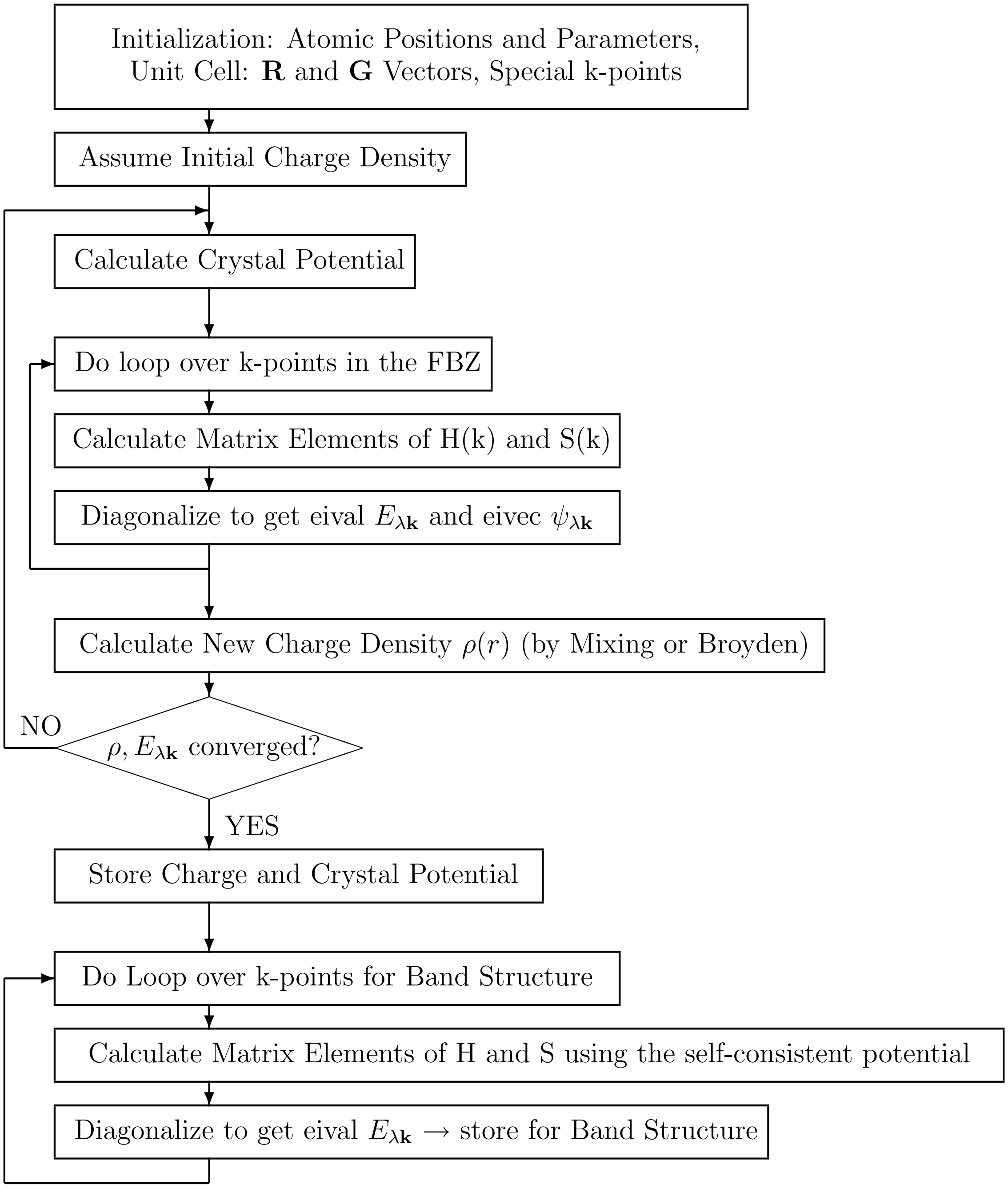
[3] typically for a k-grid not following any symmetry, $w_{\mathbf{k}} = 1/N_{\mathbf{k}}$ so that the sum is not proportional to the number of chosen k-points, and is properly normalized to the number of bands times number of spin states. In case there is a symmetry in the k-grid, different k-points might have different weights.


Initialization: Atomic Positions and Parameters,
Unit Cell: **R** and **G** Vectors, Special k-points
Assume Initial Charge Density
Calculate Crystal Potential
Do loop over k-points in the FBZ
Calculate Matrix Elements of H(k) and S(k)
Diagonalize to get eival $E_{\lambda\mathbf{k}}$ and eivec $\psi_{\lambda\mathbf{k}}$
Calculate New Charge Density $\rho(r)$ (by Mixing or Broyden)
NO
$\rho, E_{\lambda\mathbf{k}}$ converged?
YES
Store Charge and Crystal Potential
Do Loop over k-points for Band Structure
Calculate Matrix Elements of H and S using the self-consistent potential
Diagonalize to get eival $E_{\lambda\mathbf{k}}$ → store for Band Structure