Chapter I:

Adiabatic Approximation : Born-Oppenheimer

Review of Bloch theorem

Wannier Orbitals

Tight binding Approximations.

In quantum mechanics-I, we studied the quantum theory of H-atom, basically the quantum theory of a single electron in a nucleus. This was one of those rare problems which we could solve exactly, and we found that the wavefunction of the electron has well-defined orbital symmetries - which was the result of the spherical symmetry of the problem. The symmetry was that two of the angular variables θ and ϕ are periodic, ie, the wavefunction must come back to itself as $\theta \rightarrow \theta + \pi$ and $\phi \rightarrow \phi + 2\pi$. But wavefunction being complex valued, its amplitude and phase both must return to itself. The periodicity of ϕ-variable yields a wave function in which ϕ goes into the phase part only as $e^{im\phi}$, where m is quantized due to the periodic boundary condition on ϕ. We know all about this wavefunction and the quantized angular momentum $m\hbar$ for this periodic wavefunction.

Next in quantum mechanics-II, we studied He-atom problem, which has two electrons in the atom. This introduces an additional term in the Hamiltonian, which is the electron-electron interactions $\frac{e^2}{r}$. Due to this form the standard separation of variable method for the total wavefunction $\psi(\vec{r}_1, \vec{r}_2) \sim \psi(\vec{r}_1)\psi(\vec{r}_2)$, where $\psi(\vec{r}_i)$ are the individual electron's wavefunctions, does not exactly work. Rather, one takes such a wavefunction as a trial wavefunction and solve for it using the variational approximation in which the individual electron's wavefunction are varied from its form in a single-electron Hydrogen atom wavefunction. This was the Hartree-approximation. This turned out to be not such a good trial wavefunction for two reasons: this particular form of the wavefunction does not allow the single-electron wavefunctions to overlapp, and

Secondly, the fermion's exchange statistics (Pauli's exclusion principle) is not included in this wavefunction. Fock improved this trial wavefunction by considering the Slater determinant wave function which allowed the individual wavefunction to overlap (Fock / exchange term) and also the wave function is antisymmetric under the exchange of identical electrons between the two wavefunctions. For the He-atom, this wave function looks like $\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_1(\vec{r}_1)\,\psi_2(\vec{r}_2) - \psi_1(\vec{r}_2)\,\psi_2(\vec{r}_1)\right]$. Although the result was still not accurate, but it gave a much better agreement to the ground state energy.

In condensed matter physics, we deal with $\sim 10^{23}$ atoms, with each atom having Z number of electrons. Generally speaking, such a large number of atoms give three states of matter, namely the gas, liquid and solid. We will not be discussing a gas or liquid phase here, although the name "Condensed matter physics" was distinguished from the "solid state physics" subject to include the liquid phase. At the end we might be discussing a bit about the liquid, mainly the quantum liquid or superfluid phase, but primarily we will focus on the solid state physics here. In the solid phase, the atoms are periodically arranged in all d-dimension ($d=1,2,3$ are our primary focus here). In such a case we can write the full microscopic Hamiltonian as.

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{ZN}\nabla_i^2 - \frac{\hbar^2}{2M}\sum_{I=1}^{N}\nabla_I^2 + \frac{(Ze)^2}{2}\sum_{I,J=1}^{N}\frac{1}{|\vec{R}_I - \vec{R}_J|} - Ze^2\sum_{i,I}\frac{1}{|\vec{r}_i - \vec{R}_I|}$$

$$+ \frac{e^2}{2}\sum_{i,j}\frac{1}{|\vec{r}_i - \vec{r}_j|} \quad — ①.$$

Here, $\vec{R}_I$ are the positions of the I^{th} nucleus, and $\vec{r}_i$ are the same for the i^{th} electron, and we assumed N-atoms in this solid with the atomic number Z. This is actually the complete Hamiltonian of a condensed matter problem (i.e., we do not care about what's inside a nucleus). We ignore spin of the electron here, and also coupling to external electric/magnetic fields are not considered. This Hamiltonian cannot be solved exactly, due to the presence of each of the potential energy terms. The Slater determinant and separation of variables ansatz also fail miserably. In this course, we will learn a few new methods to either approximate the wave function and/or the Hamiltonian itself.

Symmetries of crystals.

Before we plunge into different methods to solve eq(1), there is one important symmetry of the problem that we need to consider here. This is the discrete lattice translational symmetry, and the discrete rotational symmetry. These are the two important symmetries that a many-body system has broken in the formation of the crysal of the system.

Discrete translational symmetry : As the atoms form a crystal, the system breaks the continuous translational symmetry to a set of discrete translational symmetry which depends on one of the 14 Bravais lattice (+ basis) that the system assumes. Here the momentum is no longer conserved, but it is conserved modulo the reciprocal lattice vector. Therefore, instead of a simple plane wave basis which one choses for system with continuous translational symmetry, Bloch (1928) proposed a modified basis, called the Bloch wavefunction. We will review it in the next chapter.

Discrete rotational symmetry: Similarly, in a solid, the continuous rotational symmetry that a single atom or gas/liquid enjoy is broken to discrete rotational symmetry. For example, in a cubic lattice, the system comes back to itself by a $2\pi/4$ rotation with respect to all three axes. Therefore, the angular momentum is not a conserved quantity, and therefore, the spherical Harmonics basis will no longer work here.

Point Group symmetries : In fact, in addition to the discrete rotational symmetries, there are also other discrete spatial symmetries that a lattice enjoys, e.g. inversion, mirror/reflection symmetries. These symmetries are sometimes called improper rotations, as they require the changes in the handedness of the reference frame. But the discrete rotations are proper rotation. Interestingly, the discrete rotation and reflection symmetries together form a closed group in a given lattice, called the point group. All the point groups of the Bravais lattices are classified, and there exist 32 crystalographic point group in nature.

To expand it further, one combines the point group with the discrete translational and other symmetries to define something called the space group symmetries. There are a total of 230 unique space groups that define all crystals in three dimensions.

The wave function of the many body Hamiltonian (eq(1)), must respect all these symmetries. Such wavefunctions which respect all the symmetry operations of a group are called irreducible representation of group. In other words, the knowledge of the space group of a lattice gives key information to the wavefunction ansatz of the lattice Hamiltonian we want to solve. This is however a very daunting task and cannot be covered in this course. Such irreducible representation of the wavefunction are considered in the numerical methods such as density functional theory (DFT), and also in low-energy theories - such as tight binding models. In this course, we will only take into account the discrete translational symmetries.

Adiabatic Approximation: Before we employ the symmetry properties of the lattice, we need to make a few other "practical approximations" to eq(1). A key set of approximations is to ignore the kinetic energy of the "immobile" particles.

(i) The nucleons are much more heavy compared to electrons, and hence its velocity should be very slow. So, we can ignore the kinetic energy of nucleons. But we also know that nucleons are vibrating around its equilibrium position. So, what we are essentially going to do is to ignore the time-dependence of the equilibrium position of the nucleons. We will solve the remaing Hamiltonian and then treat the vibration of the nucleons as perturbation. This method works as long as the there is no level crossings due to the perturbation, i.e., as long as the "adiabatic theorem" holds. This is known as the "Born-Oppenheimer approximation".

- When do we call call an approximation adiabatic ?

  If the energy levels without and with the approximation do not change except shifts in energy values, but no level crossings, then the approximation is called adiabatic. Therefore, the Born-Oppenheimer approximation may break down if electron-phonon coupling is very strong.

H.W. Assuming the nucleons making harmonic motion with a bound on its amplitude being of the order of the lattice constant, find the ratio between the fermi velocity of electrons and that of ions.

(ii) We also assume that not all electrons's wavefunction overlap with those from the nearest atoms, but only the outermost orbitals do. These outmost orbitals make up the valence and conduction bands, ei, their eigenenergies lie near the fermi level. Most of the physical properties of a material are governed by these conduction and valence electrons. The other electrons near the nucleous are tightly bound to the nucleous - they are called the "core" electrons.

How many "core" electrons one has in an atom in a lattice. This entirely depends on the characteristic of the lattice, its structure and lattice constant and one needs to find it out via trials.

So, the idea is that nucleous and core electrons move together. So we consider them as a single ion with effective positive charge of $Z-Z_c$, where Z_c is the number of core electrons. The mass of the ion is taken to be same as the mass of the nucleous. The outermost valence and conduction electrons hence experience an effective coulomb interaction due to $(Z-Z_c)$ positive charge.

Born-Oppenheimer (Adiabatic) Approximation:

Ref: A. Szabo, N. O. Ostlund, Modern Quantum Chemistry.
P. Phillips, Advanced Solid State Physics.

The Born-Oppenheimer (BO) approximation is that, we neglect the K.E. of nucleons, ie, the 2nd term in eq (1) and also assume that the repulsion between nuclei can be treated as a uniform background energy to the electron's perspective (ie, the expectation value of the third term of eq (1) is independent of the electron's coordinate $\vec{r}_i$).

This is very much to say that the total wavefunction Ψ of the Hamiltonian H in eq (1) can be separated into nucleons wavefunction Φ and electron's wavefunction ψ.

$$\Psi(\vec{r}, \vec{R}) = \sum_n \Phi_n(\vec{R}) \, \psi_n(\vec{r}, \vec{R}) \quad --(2)$$

Here $\vec{R} \equiv \{\vec{R}_I\}$, and $\vec{r} \equiv \{\vec{r}_i\}$, and n is the combined energy level index (combining all orbitals, spin, sublattice / basis etc as appropriate in a given system)

The electron's wavefunction ψ depends on both $\vec{r}$ as well as on $\vec{R}$ due to the fourth term. This means the electron's wavefunction will be sensitive to the arrangements of nucleons via the fourth term as it should be.

→ Φ_n & ψ_n are individually orthonormalized and from disjoint Hilbert spaces. Therefore, $\Psi(\vec{r}, \vec{R})$ in this form in eq (2) is a so-called "product state" or "unentangled state" in the since that electrons and nucleons are different entities. Their orthonormalizations are expressed as

$$\int \Phi_n^*(\vec{R})\, \Phi_m(\vec{R})\, \underbrace{d\vec{R}}_{=\prod_I d^3R_I} = \delta_{mn} . \quad \cdots (3a)$$

$$\int \psi_n^*(\vec{r}, \vec{R})\, \psi_m(\vec{r}, \vec{R})\, \underbrace{d\vec{r}}_{=\prod_i d^3r_i} = \delta_{nm} \quad \forall\ \vec{R} . \quad \cdots (3b)$$

This is to say the electron's wavefunction explicitly depend on its coordinates $\vec{r}$, but parametrically depend on $\vec{R}$.

→ Next, we substitute eq (2) in eq (1), and employ eqs (3a) & (3b) to obtain separate eigenvalue equations for the nuclei part and the electrons part.

The eigenvalue equation we want to solve is

$$H(\vec{R}, \vec{r})\, \Psi(\vec{R}, \vec{r}) = E\, \Psi(\vec{R}, \vec{r}) \quad --- (4a)$$

$$\left[T_I(\vec{R}) + T_e(\vec{r}) + V_{II}(\vec{R}) + V_{Ie}(\vec{R}, \vec{r}) + V_{ee}(\vec{r}) \right] \sum_n \Phi_n(\vec{R})\, \psi_n(\vec{R}, \vec{r}) = E \sum_n \Phi_n(\vec{R})\, \psi_n(\vec{R}, \vec{r}) \quad \cdots (4b) .$$

$$(T_I + V_{II}) \sum_n \Phi_n \psi_n + \sum_n \Phi_n(\vec{R}) \underbrace{\left[T_e + V_{Ie} + V_{ee} \right] \psi_n(\vec{R}, \vec{r})}_{E_{e,n}(\vec{R})\, \psi_n(\vec{R}, \vec{r})}$$

$$= E \sum_n \Phi_n \psi_n \quad --- (4c) .$$

- We first seperate the electronic part into an eigenvalue equation at every value of $\vec{R}$ as

$$\boxed{\left[T_e(\vec{r}) + V_{Ie}(\vec{R},\vec{r}) + V_{ee}(\vec{r})\right]\psi_n(\vec{R},\vec{r}) = E_{e,n}(\vec{R})\psi_n(\vec{R},\vec{r}), \forall \vec{R}. \quad -(5a).}$$

Then we are left with the nucleous part as

$$\sum_n \left(T_I(\vec{R}) + V_{II}(\vec{R}) + E_{e,n}(\vec{R}) - E\right]\Phi_n(\vec{R})\psi_n(\vec{R},\vec{r}) = 0. \quad --(5b)$$

This equation does not involve the electronic coordinates, therefore, we can get rid of the $\psi_n(\vec{R},\vec{r})$ part by using its orthonormalization condition (eq(3b)) as

$$\text{1st term}: \sum_n \int \psi_m^*(\vec{R},\vec{r})\left(-\frac{\hbar^2}{2M}\sum_I \nabla_I^2\right)\left(\Phi_n(\vec{R})\psi_n(\vec{R},\vec{r})\right) d\vec{r}.$$

Usually, the electrons are itinerant/delocalized, and its long-wavelength states lie in the low-energy spectrum of our interest. Nuclei do not move much, so for small change of R, electronic wavefunctions do not change much. So, we set $\nabla_I\psi \to 0$.
Then ∇_I^2 operator only acts on Φ_n part we get

$$= \sum_{n,I} -\frac{\hbar^2}{2m}\nabla_I^2\Phi_n(\vec{R}) \underbrace{\int \psi_m^*(\vec{R},\vec{r})\psi_n(\vec{R},\vec{r})\, d\vec{r}}_{\delta_{mn}.}$$

$$= -\frac{\hbar^2}{2m}\nabla_I^2\Phi_m(\vec{R}).$$

2nd term: $\sum_n \underbrace{\int \psi_n^*(R,r)\, \psi_m(R,\vec r)\, d\vec r}_{\delta_{nm}} \; V_{II}(\vec R)\, \Phi_n(\vec R) = V_{II}(\vec R)\, \Phi_m(\vec R)$

3rd term: $E_m(\vec R)\, \Phi_m(\vec R)$

4th term: $E\, \Phi_m(\vec R)$

Collecting them together we get an eigenvalue equation for the nucleons as

$$\boxed{\left(T_I + V_I + E_{e,m}\right) \Phi_m = E\, \Phi_m(\vec R).} \quad \text{--- (5b)}$$

where $E \equiv E_m$ the total Hamiltonian, which turns o to the eigenvalue of nucleons part also. This is the BO approximation. In this c , w tre $E_{e,m}(\vec R)$ as the effective o to the nu ons due to the electronic degrees of free

I. We will solve eq (5b) separately to obtain the lattice-vibrational, ie, phonon dispersion.

II. We will solve eq (5a) separately, by fixing the nucleons at its equilibrium positions $\vec R = \vec R_0$ such that $V_{I,e}(\vec R, \vec r) = V_{I,e}(\vec R_0 - \vec r)$ becomes an effective periodic potential to the electrons. Then solutions of eq (5a) gives us the electronic structure or the so called band structure of the lattice

III. Finally, we study electron-phonon coupling by allowing the lattice vibration and manipulating the $V_{I,e}(\vec R - \vec r)$ term.

H.W. 1. Obtain spin-orbit coupling term by deriving an electric field from the V_{Ie} potential and the magnetic field in the electronic reference of frame.

Review of Electronic Structure:

We have studied the case II in details in CMP-I course.

We rewrite eq(5a) explicitly as

$$\sum_n \left[-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - Ze^2 \sum_{I,i} \frac{1}{|\vec{r}_i - \vec{R}_I|} + \frac{e^2}{2}\sum_{i,j}\frac{1}{|\vec{r}_i - \vec{r}_j|}\right] \Phi_n(\vec{R})\,\psi_n(\vec{r},\vec{R})$$

$$= \sum_n E_{e,n}\,\Phi_n(\vec{R})\,\psi_n(\vec{r},\vec{R})$$

Multiply with $\int \Phi_n^*(R)\, d^3R$ from the left. First, and third term on L.H.S and the RHS do not have operator depending on $\vec{R}$, and hence Φ easily drops out due to orthogonality. For the second term, we define a electron-ion interaction potential as

$$v_{Ie}(\vec{r}_i) = Ze^2\int d^3R \sum_I \frac{1}{|\vec{r}_i - R_I|}\,\Phi_n^*(\vec{R})\,\phi(\vec{R}).$$

This electron-ion interaction potential is "local", ie, only depends on the electron's own coordinate, and do not cause two different electrons to interact (unless we make the nucleons move, which gives electron-phonon coupling and attractive electron-electron interaction that we will study in chapter 7). But the most important part of this potential is that its not invariant under continuous translational symmetry, but its invariant under discrete translational symmetry which we will consider below.

With this, the electronic eigenvalue equation for each n-state becomes,

$$\left[\underbrace{-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i v_{Ie}(\vec{r}_i)}_{=\sum_i h_e(\vec{r}_i)} + \frac{e^2}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|}\right]\psi_n(\vec{r},\vec{R}) = E_{e,n}\psi_n(\vec{r},\vec{R}) \quad \text{--- (6)}$$

Potential energy $V(\vec{r})$

(non-interacting electronic Hamiltonian)

where $h_e(\vec{r}_i)$ is a part of the Hamiltonian which is completely independent electron Hamiltonian, and the 2nd part of the Hamiltonian is the electron-electron interaction. This electron-electron interaction part makes the problem unsolvable exactly, but gives all sorts of interesting low-energy, low-temparature physics that we will study in this course. We will learn various approximations to solve it.

Discrete translational symmetry of the lattice :

A translational symmetry means, if we translate all the coordinates by a constant value, ie, $\vec{r}_i \to \vec{r}_i + \vec{r}$, the system remains invariant. Does that hold here in eq (6a) for any value of $\vec{r}$? The answer is NO.

- The kinetic energy in the form of $\frac{p_i^2}{2m}$ is always translationally invariant as it commutes with the momentum operators p_i.
- The electron-electron interaction part $\sim |\vec{r}_i - \vec{r}_j|$ is also translationally invariant as the shift '$\vec{r}$' drops out from the subtraction. This is to say the electron-electron interaction depends on the relative position between them, not the absolute position or not on the center of mass coordinate. This also implies that the momentum remains conserved in the electron-electron interaction, ie, the total momentum of incident electrons and final electrons after the interaction are the same.
- But the electron-nuclei interaction is not invariant to the translation of the electron's coordinate, while the nucleus remains fixed at $\vec{R}_i^0$.

- On the other hand, the Hamiltonian is invariant under the discrete translation by a fixed value of $\vec{R}_i^0$, which are the nucleus positions or the primitive lattice vectors. Therefore, the system has discrete translational symmetry if the nuclei are fixed at the lattice sites.

⊛ **Free-electron-Gas-model:** As the name "Gas" suggests, in this approximation, there is no lattice, ie, there are continuous translational and rotational symmetries in He, ie., in $V_{Ie}(r_i)$. This is roughly true for long-wavelength electrons whose wave vectors k are very small, or the wavelength $\lambda = \frac{2\pi}{k} >> a$, where a is the lattice constant. In this case, $V_{Ie}(\vec{r}_i)$ is roughly a constant ($\vec{r}$- independent) potential which can be subtracted off from the Hamiltonian. Then the Hamiltonian only has the Kinetic energy part and this can be solved by a simple Fourier transformation

$$\psi_n(\vec{r}) = \left(\frac{L}{2\pi}\right)^3 \int d^3k \, \psi_{e,n}(\vec{k}) \, e^{i\vec{k}\cdot\vec{r}} \qquad -(7a)$$

where the wavevector k ranges from $-\infty$ to $+\infty$, ie, one does not have a Brillouin zone here. The energy eigenvalues are

$$E_{n,k} = \frac{\hbar^2 k^2}{2m} + \text{Constant.} \qquad -(8a)$$

This energy is unbounded above and requires cut-off in some of the integration (not to be discussed here).

⊛ Lattice model of independent particles: The next simplest model is to invoke the discrete transational symmetry of the lattice, owing to periodic arrangements of the nuclei at $\vec{R}_I^0$ (fixed). This makes the effective potential v_{Ie}, and the Hamiltonian, to be periodic as:

$$v_{Ie}(\vec{r} + \vec{R}_I^0) = v_{Ie}(\vec{r}). \qquad — (9)$$

An important comment is in order. Because, we say "independent particle", ie, the Hamiltonian is a "direct" sum of hamiltonian of individual particles $H_e = \sum_i h_e(\vec{r}_i)$, so one can say the total wavefunction should now be the "direct product" state of each particle's wavefunction: $\psi(r_1, \ldots; r_N) = \psi(\vec{r}_1)\,\psi(\vec{r}_2) \cdots \psi(r_N)$. But the above periodic boundary condition in eq (9) makes a difference. We will rather find that the momentum space state $\psi(\vec{k})$ be the eigenstate of the Hamiltonian, which is a lineare superposition of the atomic states at $\vec{r}_i$ ($\psi(\vec{r}_i)$) with equal amplitudes but they can differ by a phase. This is the so-called Bloch state in a lattice in the non-interacting or weakly interacting limit (quasiparticle in the Fermi-liquid theorem).

- In a lattice, we should not now call $\vec{r}_i$ as the position of i^{th} atom, rather the position of the i^{th} unit cell. In a unit cell, one can have more than one atoms, called basis, in general, and each atom has different orbitals and spin. All these basis, orbital and spin indices are combined in a single index 'n' which we now change to 'α' and reserve the index 'n' for the band / energy eigenvalue. So, our single particle state is now denoted by $\psi_\alpha(r_i) \equiv \psi_{i,\alpha}$, where i stands for unit cell index with α electrons in a unit cell.
- We will then do a Bloch wave expansion for the index 'i' for each α, and obtain a "local" Bloch Hamiltonian which is a $\alpha \times \alpha$ matrix at each $\vec{k}$. Diagonalization of this $\alpha \times \alpha$ Hamiltonian gives α-bands at each k.
- Now we have a finite dimensional Hilbert space of dimension $\alpha \times N$, where $N \equiv$ number of lattice sites.
- We will be able to make remarkable progress in terms of electronic structure calculation and many experimental properties by including this simple but important symmetry consideration of eq (9). For example, recall that in Drude's classical model it was scattering from the periodic potential that produced a very short mean free path ($\sim a$), and hence was responsible for the finite electrical resistance. We will now elevate this problem to quantum mechanics and through the Bloch theorem that quantum coherence makes the mean free path infinite. Hence the electric resistance is actually zero in this model for a metal with periodically ordered lattice symmetry.

Bloch Theorem: Unlike in the free electron gas model, where the momenta $\hbar k$ is conserved due to continuous translational symmetry, in a lattice with discrete translational symmetry the momentum is now conserved modulo the reciprocal lattice vector $\vec{G}$. Mathematically, we write it as

$$\Delta\vec{k} = \vec{G}.$$

In the continuous symmetry case, the translation operator $T_{\vec{r}}$, which translates the system by $\vec{r}$, where $\vec{r}$ is a continuous length, is $T_{\vec{r}} = e^{i\frac{\vec{p}\cdot\vec{r}}{\hbar}}$. For the discrete case, only discrete operator $T_{\vec{R}_0}$ commutes with the Hamiltonian, where

$$T_{\vec{a}} = e^{i\vec{k}\cdot\vec{a}}$$

, where $\vec{R}_0=\vec{a}$ is the primitive lattice vector (there are three such lattice vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ in a 3D lattice and correspondingly three translational operators, and we denote $T_{\vec{a}}$ as a general case). Under this translation, the wave function transform as

$$T_{\vec{a}}\,\psi_\alpha(\vec{r}_i) := \psi_\alpha(\underbrace{\vec{r}_i+\vec{a}}_{\vec{r}_{i+1}=\vec{r}_i+\vec{a}}). \quad \cdots (9a)$$

Applying $T_{\vec{a}}$, N number of times, where N is the total number of unit cell, ie, $\vec{L} = N\vec{a}$ = length of the system, we obtain

$$T_{N\vec{a}}\,\psi_\alpha(\vec{r}_i) = \psi_\alpha(\vec{r}_i+N\vec{a}) = \psi_\alpha(\vec{r}_i),$$

where we impose a periodic boundary condition that the wave function comes to itself on both sides of the lattice. Hence it is easy to see that the translation only adds a phase to the wave function such that the total phase for $N\vec{a}$ translation is 2π.

This can be explicitly proved by going to the eigenstates of H. Because $[H, T_{\vec{a}}]$, so both operators have the same eigenstates. We assume $\psi_\alpha(\vec{k})$ are the eigenstates of H, and that of $T_{\vec{a}}$. Now, since $T_{\vec{a}}$ is a unitary operator, its eigenstate is a pure phase. We assume $T_a \psi_\alpha(\vec{k}) = e^{i\phi_{k,\alpha}(a)} \psi_\alpha(\vec{k})$. Then

$$T_{N\vec{a}} \psi_\alpha(\vec{k}) = e^{i\phi_{k,\alpha}(N\vec{a})} \psi_\alpha(\vec{k}) = e^{iN\phi_{k,\alpha}(\vec{a})} \psi_\alpha(k)$$

$$= \psi_\alpha(\vec{k}), \text{ due to periodic boundary condition.}$$

Therefore, $N\phi_{k,\alpha}(\vec{a}) = 2\pi$

or, $$\phi_{k,\alpha}(\vec{a}) = \frac{2\pi}{N} = \frac{2\pi}{L} a = \vec{k}_0 \cdot \vec{a}, \quad \forall \alpha.$$

where k_0 is now the minimum wave number possible, and all the wavenumbers are now integer multiple of $2\pi/L$:

$$k = \frac{2\pi}{L}\nu, \quad \nu \in \mathbb{Z} \text{ goes from } -N/2 \text{ to } N/2.$$

In other words, the wavelength / wavevector in a discrete lattice takes discrete value $\frac{2\pi}{L} \leq k \leq \frac{2\pi}{a} = \frac{2\pi N}{L}$. $N \sim 10^{23}$, and hence for practical purposes, k acts as continuous variable. Generalizing this to 3D, we get $\phi_{n,\vec{a}} = \vec{k}\cdot\vec{a} = \frac{2\pi n}{N} a$.

- Therefore, we have $T_{\vec{a}} \psi_\alpha(\vec{k}) = e^{-i\vec{k}\cdot\vec{a}} \psi_\alpha(\vec{k})$
  where we have added a '$-$' sign in the phase to be consistent with the literature, without loosing generality.
- Because, $\vec{k}$ is a good quantum number, and $\vec{k}$ is now discrete, so, we now have a finite dimensional Hilbert space, with dimension $= N\alpha$, where $N \equiv$ # of lattice sites / unit cells and $\alpha =$ # of states per unit cell, i.e., $z - z_c$ orbitals we consider.

Because, k, and α sectors of the Hilbert space are completely different, and that one cannot convert a linear momentum to orbital / spin etc, therefore these two sectors do not mix. Hence, we have a Hilbert space which can be decomposed as

$$|k,\alpha\rangle = \underset{\text{dim } N}{\underset{\uparrow}{|k\rangle}} \otimes \underset{\text{dim } \alpha.}{\underset{\uparrow}{|\alpha\rangle}}$$

In the Hamiltonian operator also, these two sectors decouple, and one has a $\alpha \times \alpha$ matrix form of the Hamiltonian at each k, ie, its block diagonal in the k-dimension, which happens due to the discrete translational symmetry. This $\alpha \times \alpha$ Hamiltonian $H(k)$ is called the Bloch Hamiltonian as derived below.

Bloch States:

- Now, since both position & momentum space are now discrete, we do a discrete Fourier transformation:

$$|k,\alpha\rangle = \frac{1}{\sqrt{N}} \sum_i e^{i \vec{k}\cdot\vec{r}_i} |\vec{r}_i,\alpha\rangle. \quad \text{---} (10).$$

Here $\vec{r}_i$ is the position of α-state in the i^{th} unit cell. This coordinate we decompose as $\vec{r}_i = \vec{r} + \vec{R}_i$, where $\vec{r}$ is the position of α-orbital within the i^{th} unit cell which is positioned at $\vec{R}_i = i\vec{a}$ with respect to the chosen origin. In this way, $\vec{r}$ is restricted to be $0 \leq \vec{r} \leq \vec{a}$, or in other words $\vec{r}+\vec{a} \sim \vec{r}$, where '$\sim$' is called equivalence relation.

Then we get from eq ⑩ :

$$|k,\alpha\rangle = \frac{1}{\sqrt{N}} \sum_i e^{i\vec{k}\cdot\vec{r}} \cdot e^{i\vec{k}\cdot\vec{R}_i} \, |\vec{r}+\vec{R}_i,\alpha\rangle .$$

Now, projecting the abstract states in the position space $\langle\vec{r}|$ on both sides we get

$$\underbrace{\langle r|k,\alpha\rangle}_{\psi_{k,\alpha}(\vec{r})} = e^{i\vec{k}\cdot\vec{r}} \, \underbrace{\frac{1}{\sqrt{N}} \sum_i e^{i\vec{k}\cdot\vec{R}_i} \underbrace{\langle\vec{r}|\vec{r}+\vec{R}_i,\alpha\rangle}_{\substack{w_{i,\alpha}(\vec{r}) \\ \text{called wannier orbitals}}}}_{\substack{u_{k,\alpha}(\vec{r}) \\ \text{called Bloch states}}}$$

With this definition, we get the Bloch wave function as

$$\boxed{\psi_{\vec{k},\alpha}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \, u_{\vec{k},\alpha}(\vec{r}).} \quad — ⑪ .$$

where $u_{k,\alpha}(\vec{r})$ are periodic as $u_{k,\alpha}(\vec{r}+\vec{a}) = u_{k,\alpha}(\vec{r})$. The wannier orbitals are the discrete fourier transformation of the Bloch states $u_{k,\alpha}(\vec{r})$:

$$w_{i,\alpha}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_k e^{-i\vec{k}\cdot\vec{R}_i} \, u_{k,\alpha}(\vec{r}) \quad \text{--(12a)}$$

$$= \frac{1}{\sqrt{N}} \sum_k e^{-i\vec{k}\cdot(\vec{r}+\vec{R}_i)} \, \psi_{k,\alpha}(\vec{r}). \quad \text{---(12b)}$$

H.W. show that despite $u_{k,\alpha}(\vec{r})$ are orthogonal states, $w_{i,\alpha}(\vec{r})$ are not always orthogonal. Under what condition $w_{i,\alpha}(\vec{r})$ become orthogonal states?

Bloch Hamiltonian: Now, we want to show that the electronic Hamiltonian, which is not diagonal in the real space Hilbert space $|\vec{r}_i, \alpha\rangle$ in both $|r_i\rangle$ & $|\alpha\rangle$ subspaces, becomes diagonal in the momentum space Hilbert space $|\vec{k}, \alpha\rangle$ in momentum state $|k\rangle$, but not necessarily in $|\alpha\rangle$ states.

To prove that this is not the case and we obtain the matrix-element of the non interacting Hamiltonian $h_e(\vec{r}_i) = T_e(\vec{r}_i) + v_{Ie}(\vec{r}_i)$ between two different orbitals and two different momentum states as $\langle k, \alpha | h_e | k', \beta \rangle$. Note that both the K.E. term T_e & the potential energy v_{Ie} in the form written above are for the continuous variable $\bar{r}_i$. But since they are both periodic functions, we can Fourier transform in terms of reciprocal lattice vector $\vec{G}$ as (omit the index 'i' for simplicity)

$$T_e(r) = \sum_G T_e(G)\, e^{i\vec{G}\cdot\vec{r}}, \quad V_{Ie}(r) = \sum_G v_{Ie}(G)\, e^{i\vec{G}\cdot\vec{r}},$$

where $\vec{G}$ runs over all possible reciprocal vectors.

Repeat the same expansion for the Bloch states

$$\left.\begin{aligned} u_{k,\alpha}(\vec{r}) &= \sum_G e^{i\vec{G}\cdot\vec{r}}\, u_{k,\alpha}(\vec{G}) \\ &= \sum_R e^{i\vec{k}\cdot\vec{R}}\, w_{R,\alpha}(\vec{r}) \end{aligned}\right\} \text{Both are equivalent but in different basis states.}$$

(H.W.) Now, write an eigenvalue equation in terms of $u_{k,\alpha}(\vec{G})$.
[Ref. page 137-139 of Ashcroft-Mermin book.]

• Wannier orbitals :

We introduced above the wannier orbitals as the discrete Fourier transformation of the Bloch states in eqs (12):

$$w_{i,\alpha}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{k} e^{-i\vec{k}\cdot\vec{R}_i}\, u_{k,\alpha}(\vec{r}) \quad \cdots (13a)$$

$$= \frac{1}{\sqrt{N}} \sum_{k} e^{-i\vec{k}\cdot(\vec{R}_i+\vec{r})}\, \psi_{k,\alpha}(\vec{r}) \quad \cdots (13b)$$

[Sometimes, the wannier orbitals are defined as $w_\alpha(\vec{r}-\vec{R}_i)$. One also defines the wannier orbitals for each bands $w_{i,n}(\vec{r})$ which is often useful to derive an effective low-energy model with few relevant bands near the Fermi level.]

The Bloch states are orthogonal as

$$\int_0^{\vec{a}} d\vec{r}\; u^*_{k,\alpha}(\vec{r})\, u_{k',\beta}(\vec{r}) = \delta_{k,k'}\,\delta_{\alpha\beta} \quad \cdots \cancel{(14a)}.$$

Similarly, the wannier states are also orthogonal as:

$$\int_0^{\vec{a}} d\vec{r}\; w^*_{i,\alpha}(\vec{r})\, w_{j,\beta}(\vec{r}) = \frac{1}{N}\sum_{k,k'} \int_0^{\vec{a}} d\vec{r}\; e^{-i\vec{k}\cdot\vec{R}_i + i\vec{k}'\cdot\vec{R}_j}\, u^*_{k,\alpha}(\vec{r})\, u_{k',\beta}(\vec{r})$$

$$= \frac{1}{N}\sum_{k,k'} e^{-i\vec{k}\cdot\vec{R}_i + i\vec{k}'\cdot\vec{R}_j}\, \delta_{kk'}\,\delta_{\alpha\beta}$$

using eq (14a).

$$= \delta_{ij}\,\delta_{\alpha\beta} \quad \cdots (14b)$$

- Although it all looked consistent and that wannier states are orthogonal given that Bloch states are orthogonal, but do wannier states form a complete basis; i.e., a Hilbert space? The answer lies in its definition $w_{i,\alpha}(\vec{r}) = \langle \vec{r} | \vec{r}_i, \alpha \rangle$. The $|\vec{r}_i, \alpha\rangle$ states are discrete and orthogonalized appropriately. But $|\vec{r}\rangle$ state is continuous and is infinite dimensional. The completeness of $|\vec{r}\rangle$ states is defined for $\vec{r} = -\infty$ to ∞ as

$$\int_{-\infty}^{\infty} d\vec{r} \; |\vec{r}\rangle\langle\vec{r}| = 1.$$

But here $\vec{r}$ is restricted within a unit cell from 0 to $\vec{a}$. Therefore, strictly speaking, the wannier states may not be complete, unless $w_{i,\alpha}(\vec{r})$ states decay sufficiently fast within a unit cell that its value outside the unit cell is negligibly small. In numerical computations, the wannier orbitals are constructed such that they are confined within a unit cell, and such states are called Maximally localized Wannier orbitals.

H.W.
- Wannier states are clearly not the eigenstates of the position operator $\vec{r}$. The uncertainty in position in a wannier state $(\Delta r)_0^2 = \sum_\alpha \left[\langle 0,\alpha | r^2 | 0,\alpha\rangle - \langle 0,\alpha | r | 0,\alpha\rangle^2\right]$, where $|0,\alpha\rangle = |\vec{r}_i = 0, \alpha\rangle$. The idea is to minimize $\Delta r < a$.
- Show that the wannier states are the eigenstate of this "position" operator $\hat{x} = \sum_i e^{i\vec{k}_0 \cdot \vec{R}_i} |i,\alpha\rangle\langle i,\alpha|$, where $k_0 = \frac{2\pi}{L}$. Find the corresponding eigenvalues.

- ## Tight binding model.

We can express the electronic Hamiltonian in the matrix form in the wannier basis - this is called the tight binding model. We assume the maximally localized wannier states such that they form a complete basis and we have $\sum_{i,\alpha} |i,\alpha\rangle\langle i,\alpha| = \mathbb{I}$. Then we obtain

$$H_e = \sum_{\substack{i,\alpha \\ j,\beta}} |i,\alpha\rangle\langle i,\alpha| H_e |j,\beta\rangle\langle j,\beta| \quad , \text{ where } H_e \text{ does } \underline{\text{not}} \text{ include e-e interactions}$$

$$= \sum_{ij,\alpha\beta} H_{ij}^{\alpha\beta} |i\alpha\rangle\langle j\beta| \quad , \text{ where } H_{ij}^{\alpha\beta} = \langle i\alpha| H_e |j,\beta\rangle \qquad -(15)$$

In this approximation, we often restrict ourselves to nearest neighbor (NN), next - nearest neighbor (NNN), and so on terms and use these matrix elements as parameters (called the tight binding parameters) to fit the band structure to experiment and / or to the one obtained in more sophisticated numerical method such as the density functional theory (DFT). Traditionally, these parameters are denoted as

$$t_{\alpha\beta} = - \langle i,\alpha| H_e | i+\delta, \beta\rangle \; ,$$
$$t'_{\alpha\beta} = - \langle i,\alpha| H_e | i+\delta', \beta\rangle \; , \text{and so on.}$$

and the onsite term as

$$E^0_{\alpha\beta} = \langle i,\alpha| H_0 | i, \beta\rangle .$$

Here, δ, δ' run over the number of NN, NNN atoms.

Then the Hamiltonian reads as

$$H_e = \sum_{i,\alpha\beta} E^0_{\alpha\beta} \, |i,\alpha\rangle\langle i,\beta| \; - \sum_{\langle ij\rangle,\alpha\beta} t_{\alpha\beta} \, |i,\alpha\rangle\langle j,\beta\rangle$$

$$- \sum_{\langle\langle ij\rangle\rangle,\alpha\beta} t'_{\alpha\beta} \, |i,\alpha\rangle\langle j,\beta| + \cdots \quad \text{--- (16)}$$

where $\langle ij\rangle$ symbol is traditionally used to denote that j is restricted to the nearest neighbors of i. Similarly for $\langle\langle ij\rangle\rangle$.

Then we use the Fourier transformation in eq (12a)

$$|i,\alpha\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-i\vec{k}\cdot\vec{R}_i} \, |k,\alpha\rangle$$

and substitute in eq (16) to obtain:

$$H_e = \sum_{\alpha\beta} h_{\alpha\beta}(k) \, |k,\alpha\rangle\langle k,\beta| \quad \text{--- (17).}$$

which is diagonal in the momentum space, with the matrix elements obtained as

$$h_{\alpha\beta}(k) = E^0_{\alpha\beta} - t\sum_{\delta} e^{i\vec{k}\cdot\vec{\delta}} - t'\sum_{\delta'} e^{i\vec{k}\cdot\vec{\delta}'} \quad \text{--- (18)}$$

Finally, we diagonalize $h_{\alpha\beta}(k)$ at each k to obtain the band dispersion.

→ Slater-Koster evaluated these terms for different orbital symmetries $|\alpha\rangle$ and in different lattices. They are called Slater-Koster tight binding parameters.