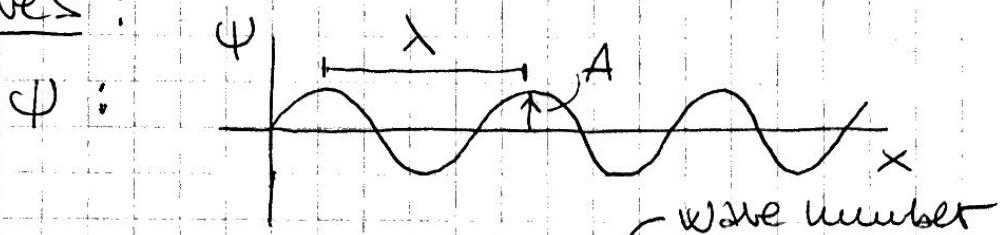


Schrödinger equation 101

Facts:

- 1) any particle system (electron, proton etc.) behaves as a beam of waves
- exp.: diffraction / interference of particle beams
- 2) atoms are photons + electrons systems
- 3) electrons in atoms cannot have a continuous distribution of energies
they are allowed only discrete values \rightarrow quantized (quantization of energy levels)
- exp.: excitation spectra of atoms show discrete lines

Waves:



$$\Psi = A \sin[2\pi(kx - vt)]$$

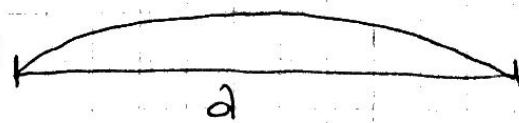
λ = wave length $= \frac{1}{k}$ phase

v = frequency

$v = \text{velocity} = \lambda v \rightarrow$ wave moves left to right with velocity v

* Right to left would be $\Psi = A \sin[2\pi(kx + vt)]$

A superposition of Ψ^{RL} and Ψ^{LR} will give rise to a standing (stationary) wave \rightarrow oscillations possible between fixed points (ringing in musical instrument)



1st mode $\frac{1}{2}\lambda = a$ and
 $v = \frac{\lambda}{T} = \frac{\lambda}{2a}$

Vibrations are allowed only for $\frac{1}{2}n\lambda = a$ with

$$\nu_n = \frac{nv}{2a} \rightarrow \text{normal modes and characteristic frequencies}$$

Example

electrons confined in a box

If the electrons are described by a wave equation $\Psi \rightarrow$

$\Psi = 0$ for $x=0$ and $x=a$ \Rightarrow must be a standing wave \Rightarrow

$$\begin{aligned}\Psi &= \sin(2\pi(kx - vt)) + \sin(2\pi(kx + vt)) = \\ &= 2 \sin(2\pi kx) \cos(2\pi vt)\end{aligned}$$

For the condition to be true $\Rightarrow 2\pi ka = n\pi$ or

$$k = \frac{2a}{n}$$

Fact

An electron is described by a wave with
 $\lambda = h/m_e v$ where $h = \text{Planck's constant}$
 $m_e = \text{electron mass}$.

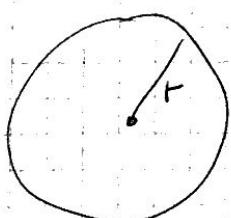
$\hookrightarrow v = \frac{nh}{2m_e a} \Rightarrow \text{kinetic energy of the electron}$

$$E = \frac{1}{2} m_e v^2 = \frac{n^2 h^2}{8m_e a^2} \quad n=1, 2, \dots$$

\hookrightarrow quantized values!

Extension To The Bohr atomic model:

Electrons orbiting around the nucleus \Leftrightarrow electrons in a box with $a = 2\pi r$.



$$e\lambda = 2\pi r \Rightarrow \text{since } \lambda = \frac{h}{mv}$$

integer number of wavelengths

fit the circumference

$$mvr = \frac{eh}{2\pi}$$

Bohr's quant. 2nd rule
of angular momentum
 $e=0, 1, 2, \dots$

and the energy $\omega = \frac{1}{2}mv^2 = \frac{e^2 h^2}{8\pi^2 m r^2} \leftrightarrow \text{quantized}$

The Schrödinger equation

A wave of the form $\psi A e^{2\pi i(kx - vt)}$ is the solution of the simple harmonic equation

$$\frac{d^2\psi}{dx^2} + 4\pi^2 k^2 \psi = 0$$

If a field $V(x)$ is present, then $k = k(x) \Rightarrow$ since

$$k^2 = \frac{\frac{m c^2 v^2}{h^2}}{h^2} = 2m_e(\omega - V)/h^2$$

2 × kinetic energy Total energy \rightarrow potential energy

we can rewrite the wave equation as

Schrödinger
equation

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m_e}{h^2} (\omega - V(x)) \psi = 0}$$

Example electron in a box $x=0$ and $x=a$

$$V(x) = 0 \rightarrow \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m_e}{h^2} \omega \psi = 0$$

again, simple wave equation \rightarrow look for solutions that vanish at $x=0$ and $x=a$

$$x=0 \rightarrow \psi = A \sin 2\pi k x$$

$$x=a \rightarrow k = \frac{n}{2a} \quad (k = \frac{1}{x}) \rightarrow$$

$$\omega = \frac{n^2 h^2}{8m_e a^2} \quad \text{as before.}$$

The harmonic oscillator

In classical mechanics (Newton), the equation of motion is $m \frac{d^2x}{dt^2} = -qx$, with a general solution $x = A \cos(2\pi\nu t + \epsilon)$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{q}{m}}, \epsilon = \text{constant.}$$

\downarrow
potential energy $V(x) = \frac{1}{2} qx^2 \Rightarrow$ Schrödinger equation can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (\nu - \frac{1}{2} qx^2) \psi = 0$$

\downarrow
The solution of this equation for the quantized energy values is

$$\nu = (n + \frac{1}{2}) \nu_0$$

\Rightarrow Energy of vibrating atoms in a solid

Note $n=0$ gives

$$\nu = \frac{1}{2} \nu_0 \rightarrow \underline{\text{zero point motion}}$$

NOTE

Hamiltonians

How do we go from the classical eq. of motion to the Schrödinger equation?

Hamiltonian equation: define Hamiltonian as a function that gives the total energy of a system \rightarrow for closed systems, is the sum of the kinetic and potential energies:

$$H = T + V = H(p, x) = \frac{p^2}{2m} + V(x)$$

momentum coordinates

Classical equations of motion are derived at
Newton's II law $F=ma$

$$\left\{ \begin{array}{l} \frac{dp}{dt} = -\frac{\partial H}{\partial x} \\ \frac{dx}{dt} = \frac{\partial H}{\partial p} \end{array} \right. \quad \begin{array}{l} \text{Hamilton} \\ \text{equations} \end{array}$$

~~velocity~~ = ~~derivative of~~
~~the kinetic~~
~~energy~~

In quantum mechanics, observable such as momentum of position are described by linear operators acting on the wavefunction Ψ :

$$P \rightarrow \hat{p} = -i\hbar \nabla \quad (\hbar = \frac{h}{2\pi})$$

$$x \rightarrow \hat{x} = x$$

Schroedinger equation becomes

$$\hat{p}^2 \psi + \frac{8\pi^2 m}{h^2} (\omega - V(x)) \psi = 0$$

$$-\nabla^2 \psi + (\omega - V(x)) \psi = 0 \quad \text{or}$$

$$H \psi - \omega \psi = 0 \quad \text{or} \quad H \psi = \omega \psi$$

\downarrow ~~eigen~~ \nwarrow ~~vector~~ \nwarrow ~~number~~

In linear algebra

This is an eigenvalue problem \equiv diagonalization

Electrons in a periodic potential: The 1-dim. case.

Consider the case of a non interacting electron gas in 1 dim. The Schrödinger equation in its general form reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x).$$

We want to specialize this to the case in which $V(x)$ is periodic with the periodicity of a 1-dim lattice (L):

$$V(x + \frac{nL}{a}) = V(x), \quad n \text{ arbitrary integer.}$$

Periodic function \Rightarrow Fourier Transform, and the condition of periodicity implies that only plane waves with wavevector

$$k_n = \frac{2\pi n}{L} \quad \text{enter in the series}$$

$$V(x) = \sum_{n=-\infty}^{+\infty} V_n e^{ik_n x}$$

If $V(x) = 0$ we know the solution of the S. eq. To be plane waves

$$\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}$$

$\psi(x)$ is normalized, k are real and $E(k) = \frac{\hbar^2 k^2}{2m}$.

What happens if the potential is periodic: $V(x) \Rightarrow$

$\hat{H} = -\frac{\hat{P}^2}{2m} + V(x)$ and let's apply it on the generic plane wave $\psi_k(x)$:

$H\psi_k(x)$ acts on the plane wave as the "confining" potential of the box in the "free" electron model \Rightarrow $V(x)$, that is periodic

$H\psi_k(x)$ belongs to the subspace of all possible plane waves that satisfy the periodicity of the

potential, that is, to the subspace of all the plane waves of the form

$$\psi_{k+k_n}(x) \text{ for arbitrary } n.$$

This is a closed subspace (H applied to any element, will produce another element of the subspace) \Rightarrow
 The diagonalization of H within the subspace provides the ~~relations of the eigenstates~~, eigenfunctions of the Hamiltonian: namely $\boxed{\psi_k(x)}$ for any ~~odd~~ ~~and k odd~~ ~~values~~

1. $\psi_k(x), \psi_{k'}(x)$ belong to the same subspace if $k' = k + \frac{2\pi}{a}n$
2. Only the region of space that is comprised between $-\frac{\pi}{a} < k < \frac{\pi}{a}$ gives rise to independent subspaces.

This fundamental region, of length $2\pi/a$ is called "first Brillouin zone".

Any generic wavefunction $\psi(x)$ can be written as a linear combination of ~~plane waves~~ the type

$$\psi_k(x) = \sum_n c_n(k) \frac{1}{\sqrt{L}} e^{i(k+k_n)x}$$

If we introduce the function $v_k(x) = \sum_n c_n(k) \frac{1}{\sqrt{L}} e^{ik_n x} (k_n = \frac{2\pi n}{a})$

Then

$$\boxed{\psi_k(x) = e^{ikx} v_k(x)}$$

\downarrow
 Due to periodicity of $V(x) \Rightarrow$

$v_k(x) = v_k(x+a)$ is periodic with the period of the lattice

Bloch Theorem

any solution of the Sch. eq. in a periodic potential has the form of a travelling wave modulated by a function with lattice periodicity

$\Psi_k(x) = e^{ikx} \psi_k(x)$ is also equivalent to

$$\boxed{\begin{aligned}\Psi_k(x+a) &= e^{ika} \Psi_k(x) \\ \Psi_k(x+t_n) &= e^{ikt_n} \Psi_k(x)\end{aligned}}$$

$a = t_n$ = Translation
in the direct lattice

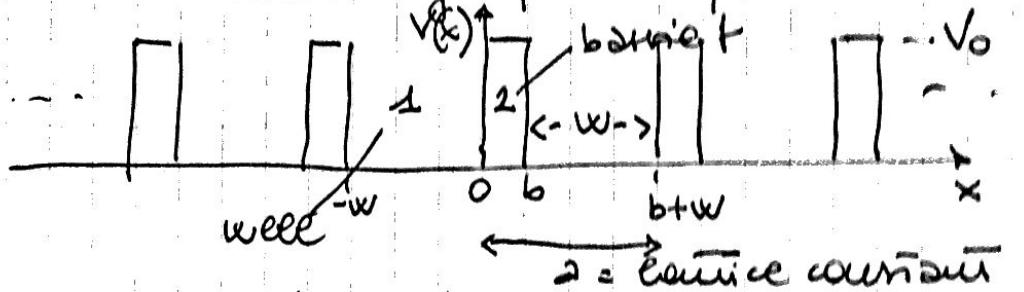
As for the allowed k vectors \Rightarrow periodic boundary conditions

$$\Psi(x) = \Psi(x+Na) \text{ for Nearest } (Na=L)$$

$$\Rightarrow e^{ikNa} = 1 \text{ or } k = \frac{2\pi n}{Na} = \frac{2\pi}{L} n \text{ integer } \geq 0.$$

Simple 1 dim periodic system: The Kronig-Penney model

Periodically repeated quantum well model



Elementary problem of QM: for the 2 regions. The general solution of the S. eq. will be

$$\begin{cases} \Psi_1(x), & -w < x < 0 \\ \Psi_2(x), & 0 < x < b \end{cases}$$

$$\begin{aligned}\Psi_1(x) &= Ae^{iqx} + Be^{-iqx} & q(E) &= \sqrt{\frac{2mE}{\hbar^2}} \\ \Psi_2(x) &= Ce^{\beta x} + De^{-\beta x} & \beta(E) &= \left(\frac{2m(V_0-E)}{\hbar^2}\right)^{1/2}\end{aligned}$$

A, B, C, D arbitrary constants chose so as to satisfy the boundary conditions of the S. eq. and the Bloch Theorem

1. continuity of ψ and its derivative at $x=0$

$$\Psi_1(0) = \Psi_2(0)$$

$$\left. \frac{d\Psi_1}{dx} \right|_{x=0} = \left. \frac{d\Psi_2}{dx} \right|_{x=0}$$

Electron levels in a periodic potential

Generalization in 3dim: $V(\vec{r} + \vec{R}) = V(\vec{r})$ for all Bravais lattice vectors $\vec{R} = n_1 \hat{\vec{z}}_1 + n_2 \hat{\vec{z}}_2 + n_3 \hat{\vec{z}}_3$.

Block Theorem:

The eigenstates of the 1-electron hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad \text{can be chosen}$$

To have the form of a plane wave times a function with the periodicity of the Bravais lattice

$$\Psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r}) \quad \text{where}$$

$$u_{n\vec{k}}(\vec{r} + \vec{R}) = u_{n\vec{k}}(\vec{r}) \quad \text{for all } \vec{R} \in BL.$$

This is also equivalent to the condition that

$$\Psi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \Psi_{n\vec{k}}(\vec{r}).$$

Proof

For each B.L. vector \vec{R} let's define a translation operator $T_{\vec{R}}$ which shifts the argument of any function $f(\vec{r})$ by \vec{R} :

$$T_{\vec{R}} f(\vec{r}) = f(\vec{r} + \vec{R}).$$

Since the hamiltonian is periodic

$$T_{\vec{R}} H \Psi = H(\vec{r} + \vec{R}) \Psi(\vec{r} + \vec{R}) = H(\vec{r}) \Psi(\vec{r} + \vec{R}) = H T_{\vec{R}} \Psi \Leftrightarrow$$

$$T_{\vec{R}} H = H T_{\vec{R}} \quad \text{or} \quad H \text{ and } T_{\vec{R}} \text{ commute.}$$

Moreover, the application of two successive translations does not depend on the order

$$T_{\vec{R}} T_{\vec{R}'} \Psi(\vec{r}) = T_{\vec{R}'} T_{\vec{R}} \Psi(\vec{r}) = \Psi(\vec{r} + \vec{R} + \vec{R}') \Rightarrow$$

$$T_{\vec{R}} T_{\vec{R}'} = T_{\vec{R}' \vec{R}} = T_{\vec{R} + \vec{R}'}.$$

If two operators commute, the eigenstates of H can be chosen so to be simultaneously eigenstates of $T_{\vec{R}}$

$$H \Psi = E \Psi$$

$$T_{\vec{R}} \Psi = c(\vec{R}) \Psi.$$

The eigenvalues $c(\vec{R})$ have to fulfill the conditions

$$T_{\vec{R}} T_{\vec{R}'} \Psi = c(\vec{R}) c(\vec{R}') \Psi$$

$$T_{\vec{R}} T_{\vec{R}'} \Psi = T_{\vec{R} + \vec{R}'} \Psi = c(\vec{R} + \vec{R}') \Psi \Rightarrow$$

From There, it follows

$$c(\bar{R} + \bar{R}') = c(\bar{R})c(\bar{R}') \leftarrow \text{opposite form}$$

If \bar{a}_i are the primitive vectors for the B.L., then $c(\bar{a}_i)$ can be always written as

$$c(\bar{a}_i) = \cancel{e}^{2\pi i \cdot \bar{x}_i}, \text{ so if } \bar{R} = u_1 \bar{a}_1 + u_2 \bar{a}_2 + u_3 \bar{a}_3$$

$$\Rightarrow c(\bar{R}) = c(\bar{a}_1)^{u_1} c(\bar{a}_2)^{u_2} c(\bar{a}_3)^{u_3} \text{ That is precisely equal to}$$

$$c(\bar{R}) = e^{i \bar{k} \cdot \bar{R}} \text{ if } \bar{k} = x_1 \bar{b}_1 + x_2 \bar{b}_2 + x_3 \bar{b}_3 \text{ and}$$

$$\bar{b}_i \cdot \bar{a}_j = 2\pi \delta_{ij} \text{ (as from the definition of reciprocal lattice).}$$

In conclusion ~~that~~ $T_{\bar{R}} \psi = \psi(\bar{r} + \bar{R}) = c(\bar{R}) \psi = e^{i \bar{k} \cdot \bar{R}} \psi$ QED.

So far we have not specified \bar{k} (That is the x_i coefficients), crystalline system \equiv periodic boundary conditions:

$$\psi(\bar{r} + N_i \bar{a}_i) = \psi(\bar{r}) \quad i=1,2,3 \text{ and}$$

$$N = N_1 \times N_2 \times N_3 \equiv \# \text{ of unit cells in the crystal}$$

If we apply the Bravais Theorem to this choice of boundary conditions we get

$$\psi_{\bar{k}}(\bar{r} + N_i \bar{a}_i) = e^{i N_i \bar{k} \cdot \bar{a}_i} \psi_{\bar{k}}(\bar{r}) \text{ which}$$

$$e^{i N_i \bar{k} \cdot \bar{a}_i} = 1 \Leftrightarrow e^{2\pi i N_i x_i} = 1 \text{ or}$$

$$x_i = \frac{m_i}{N_i} \text{ with } m_i = \text{integer.}$$

The allowed values of \bar{k} are thus

$$\bar{k} = \frac{m_1}{N_1} \bar{b}_1 + \frac{m_2}{N_2} \bar{b}_2 + \frac{m_3}{N_3} \bar{b}_3.$$

The volume of space allowed per \bar{k} point is the parallelepiped of edges $\bar{b}_i / N_i \Rightarrow$

$$\Delta \bar{k} = \frac{\bar{b}_1}{N_1} \times \left(\frac{\bar{b}_2}{N_2} \cdot \frac{\bar{b}_3}{N_3} \right) = \frac{1}{N} \underbrace{\bar{b}_1 \times (\bar{b}_2 \cdot \bar{b}_3)}_{\text{volume of the reciprocal lattice}} = \frac{V}{N}$$

That, recollecting $\Omega = \frac{(2\pi)^3}{V} N$ gives

$$\Delta \bar{k} = \frac{(2\pi)^3}{V} \quad \text{as for the free electron case.}$$

$$\Omega = \frac{(2\pi)^3}{V} \quad V = \frac{V}{N}$$

Bloch Theorem and plane waves

Start from the periodic boundary conditions \Rightarrow any function that obeys them can be expanded in a plane wave series

$$\Psi(\vec{r}) = \sum_{\vec{q}} c_{\vec{q}} e^{i\vec{q} \cdot \vec{r}}$$

Since $V(\vec{r})$ has the periodicity of the lattice, its plane wave expansion will have the vectors restricted to the reciprocal lattice vectors, \vec{G}

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}, \text{ where}$$

$$V_{\vec{G}} = \frac{1}{v} \int_{\text{cell}} d\vec{r} e^{-i\vec{G} \cdot \vec{r}} V(\vec{r}).$$

Since $V(\vec{r})$ is defined up to an arbitrary constant V_0 , we can impose the requirement that

$$V_0 = \frac{1}{v} \int_{\text{cell}} V(\vec{r}) d\vec{r} = 0$$

average over one unit cell.

Moreover, since $V(\vec{r})$ is real, the Fourier coefficients satisfy

if the crystal system has inversion symmetry

$$V(\vec{r}) = V(-\vec{r}) \Rightarrow$$

$$V_{\vec{G}} = V_{-\vec{G}} = V_{\vec{G}}^* \Leftrightarrow V_{\vec{G}} \text{ are real.}$$

Let's put this expansion in the Schrödinger eq.

$$\frac{\vec{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 \Psi = \sum_{\vec{q}} \frac{\hbar^2}{2m} q^2 c_{\vec{q}} e^{i\vec{q} \cdot \vec{r}}$$

and

$$\begin{aligned} V\Psi &= \left(\sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \right) \left(\sum_{\vec{q}} c_{\vec{q}} e^{i\vec{q} \cdot \vec{r}} \right) = \underbrace{\sum_{\vec{G}} V_{\vec{G}} c_{\vec{G} + \vec{q}}}_{\vec{G} + \vec{q} = \vec{q}'} e^{i\vec{q}' \cdot \vec{r}} \\ &= \sum_{\vec{q}} V_{\vec{G}} c_{\vec{q}} e^{i(\vec{G} + \vec{q}) \cdot \vec{r}} = \sum_{\vec{q}} V_{\vec{G}} c_{\vec{q}' - \vec{G}} e^{i\vec{q}' \cdot \vec{r}}. \end{aligned}$$

Let's call $\vec{q}' \rightarrow \vec{q}$ and $\vec{G} \rightarrow \vec{G}' \Rightarrow$

$$\sum_{\vec{q}} e^{i\vec{q} \cdot \vec{r}} \left[\left(\frac{\hbar^2}{2m} q^2 - E \right) c_{\vec{q}} + \sum_{\vec{G}} V_{\vec{G}} c_{\vec{q}' - \vec{G}} \right] = 0.$$

In order for this to be true, and since the plane

waves that satisfy the periodic boundary conditions are all orthogonal \Rightarrow all the coefficients have to be zero simultaneously.

$$\left(\frac{\hbar^2}{2m} q^2 - \epsilon \right) c_{\vec{q}} + \sum_{\vec{G}} V_{\vec{G}} c_{\vec{q}-\vec{G}} = 0.$$

Let's write $\vec{q} = \vec{k} - \vec{G}$, where \vec{k} is a wave vector that lies in the first Brillouin zone

$$\left(\frac{\hbar^2}{2m} (\vec{k} - \vec{G})^2 - \epsilon \right) c_{\vec{k}-\vec{G}} + \sum_{\vec{G}} V_{\vec{G}} c_{\vec{k}-\vec{G}-\vec{G}} = 0.$$

After removing $\vec{G} \rightarrow \vec{G} + \vec{G}$ we finally get

$$\boxed{\left(\frac{\hbar^2}{2m} (\vec{k} - \vec{G})^2 - \epsilon \right) c_{\vec{k}-\vec{G}} + \sum_{\vec{G}} V_{\vec{G}} c_{\vec{k}-\vec{G}} = 0}$$

Schrödinger equation in reciprocal space.

For any fixed \vec{k} in the FBZ. This is a set of linear equations. Then couple coefficients $c_{\vec{k}}, c_{\vec{k}-\vec{G}}, c_{\vec{k}+\vec{G}}$ etc. whose wave vectors differ from \vec{k} by a reciprocal lattice vector \Rightarrow N independent problems, one for each \vec{k} in the FBZ.

\hookrightarrow The solutions of each independent problem are superpositions of plane waves that contain only the subset $\vec{k} \pm \vec{G} = \vec{q} \Rightarrow$

$$\Psi_{\vec{k}} = \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G}) \cdot \vec{r}} \quad \text{That can}$$

be written as

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \underbrace{\sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{i\vec{G} \cdot \vec{r}}}_{\substack{\text{periodicity of} \\ \text{The Basis Lattice}}} = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r})$$

Block Theorem again.

Note This is an eigenvalue problem that for each \vec{k} has an infinite set of solutions with discretely spaced eigenvalues (same as the particle in a box problem, etc. \Rightarrow The problem is set in a finite volume \Rightarrow single primitive cell of the crystal).

Energy bands

Note Since $\Psi_{n\vec{k},\vec{G}}(\vec{r}) \cdot \Psi_{n'\vec{k}',\vec{G}'}(\vec{r}) \propto e_{n\vec{k},\vec{G}} \cdot e_{n'\vec{k}',\vec{G}'}$ also has the periodicity of the reciprocal lattice \Rightarrow continuous function.

The ground state of N free electrons is concerned by occupying all the 1-electron levels $E(k) < E_F$.

Similarly, the ground state of N Bloch electrons is concerned by occupying the states $E_{n\vec{k}}$, now defined by two quantum numbers, n and \vec{k} , with \vec{k} adapted to be single primitive cell (TBZ).

Two scenarios:

1. A finite number of bands get completely filled and there is an energy gap separating them from the unoccupied ones. Every # of electrons imbalance (conductor)
2. A number of bands get partially filled \rightarrow The Fermi surface of the free electron gas now becomes a Fermi surface.

For the bands that are partially filled draw the bands now

$$E_n(\vec{k}) = E_p$$

Definition of states

In general, we deal with quantities that are summed over electronic levels \rightarrow generalization of the free electron case

$Q = \sum_k Q_k(\vec{k}) \quad \rightarrow$ The limit of infinite crystal, we can't do it \rightarrow consider the sum as integral instead

and the density of states in a space is with the same as in real space we do

$$q = \lim_{N \rightarrow \infty} \frac{1}{V} + \sum_{k=1}^N \int_{BZ} g_k(\vec{k}) Q_k(\vec{k})$$

where we can again introduce a density of states function $g(\epsilon)$, such that

$$g(\epsilon) \rightarrow q = \int d\epsilon g(\epsilon) Q(\epsilon)$$

Now we have another quantum number, not

$$Q(\epsilon) = \frac{1}{V} g_v(\epsilon), \text{ where}$$

Weak periodic potential

Independent electrons in a weak periodic potential \rightarrow perturbation over the free electron case

1. valence electrons feel a weak nuclear potential screened by the core electrons (They cannot get close to the nuclei because of the Pauli principle)
2. valence electrons move so to screen the ionic potential that any other electron experience (screening \rightarrow far reaching implications !!)

Let's start from the Bloch function

$$\Psi_E(\vec{r}) = \sum_{\vec{k}} c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G}) \cdot \vec{r}}$$

that satisfy the schrödinger eq. in reciprocal space (linear system):

$$\left[\frac{\hbar^2}{2m} (\vec{k} - \vec{G})^2 - \epsilon \right] c_{\vec{k}-\vec{G}} + \sum_{\vec{G}'} V_{\vec{G}'-\vec{G}} c_{\vec{k}-\vec{G}'} = 0.$$

\Rightarrow 1 solution for each \vec{k} = bands

Free electron case

All $V_{\vec{G}} = 0$ and the equivalence of equations becomes

$$c_{\vec{k}-\vec{G}} \left(\frac{\hbar^2}{2m} (\vec{k} - \vec{G})^2 - \epsilon \right) = 0 \quad \text{or} \quad \frac{\epsilon^0_{\vec{k}-\vec{G}} - \epsilon}{\vec{k}-\vec{G}} = 0$$

This equation is true if either

$$c_{\vec{k}-\vec{G}} = 0 \quad \text{or} \quad \frac{\epsilon^0_{\vec{k}-\vec{G}}}{\vec{k}-\vec{G}} = \epsilon \rightarrow 2 \text{ possibilities}$$

1. only one value of \vec{G} corresponds to this equivalence

no degeneracy $\epsilon = \epsilon^0_{\vec{k}-\vec{G}}$ and $\Psi_k \propto e^{i(\vec{k}-\vec{G}) \cdot \vec{r}}$

2. more than one \vec{G} satisfy the condition

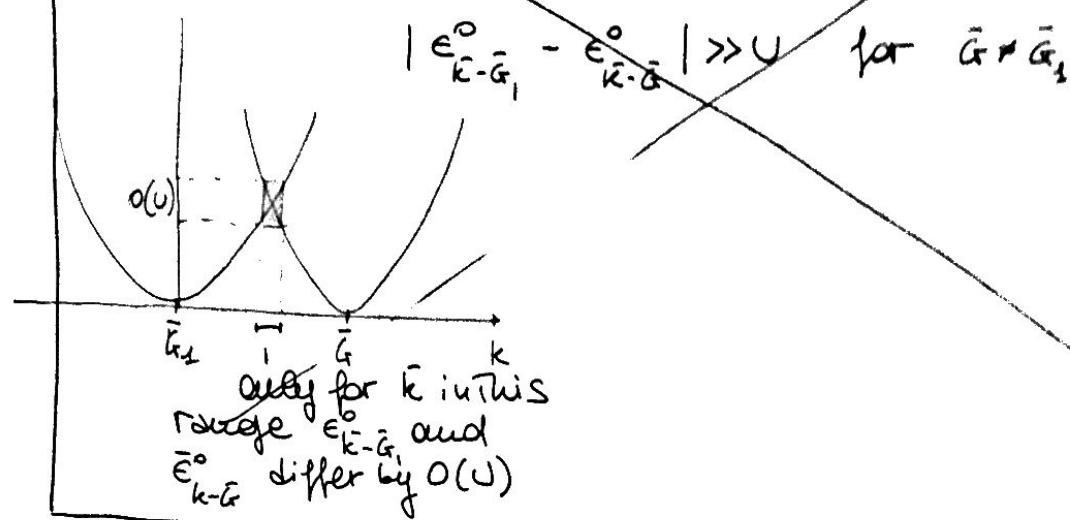
degeneracy $\epsilon^0_{\vec{k}+\vec{G}_1} = \epsilon^0_{\vec{k}+\vec{G}_2} \dots = \epsilon^0_{\vec{k}+\vec{G}_m} \Rightarrow$ There

are no degenerate plane wave solutions and since any linear combination will still be a solution, one has complete freedom in choosing the coefficients $c_{\vec{k}-\vec{G}}$ for $\vec{G} = \vec{G}_1 \dots \vec{G}_m$.

This analysis becomes more useful if the $V_{\vec{G}}$ are not zero but small.

Case 1 - no degeneracy

Fix \bar{k} and consider \bar{G}_1 such that $\epsilon_{\bar{k}-\bar{G}_1}^0$ is far from the values for all other \bar{G} , $\epsilon_{\bar{k}-\bar{G}}^0$, compared with U :



Nearly free electron approximation in 1 dim.

Start from the empty lattice solution and solve the problem for a (vanishing) periodic potential:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

At any given k The crystal wavefunction can be written as linear combination of plane waves

$$\Psi_{k+G_n}(x) = \frac{1}{\sqrt{L}} e^{i(k+G_n)x} \quad \text{where}$$

$G_n = \frac{2\pi}{a} n$ is an arbitrary reciprocal lattice vector.

We need to solve

$H \Psi_{k+G_m}(x) = \epsilon_{k+G_m} \Psi_{k+G_m}(x)$. The matrix elements of H between these basis functions are

$$\begin{aligned}
 H_{nm} &= \langle \Psi_{k+G_m}(x) | H | \Psi_{k+G_n}(x) \rangle = \frac{\hbar^2 (k+G_n)^2}{2m} \delta_{nm} + \\
 &\quad \left(+ \frac{1}{L} \int_0^L e^{-i(G_m - G_n)x} V(x) dx \right) \\
 &= \frac{\hbar^2 (k+G_n)^2}{2m} \delta_{mn} + V(G_m - G_n).
 \end{aligned}$$

$$11 \quad \left(\frac{4\pi^2 K - G_0}{2m} \right)^2 - \epsilon = \delta_{nm} + V(G_m - G_n) = \text{f}(n,m)$$

See $V(k)$ is small
are negligible

$$11 = \begin{pmatrix} \epsilon_0 - \epsilon & V(G_1) \\ V(-G_1) & \epsilon_0 - \epsilon \end{pmatrix} = \begin{pmatrix} \epsilon_0 - \epsilon & V_1 \\ V_1^* & \epsilon_0 - \epsilon \end{pmatrix}$$

$$\text{since } V(-k) = V^*(k) \cdot \begin{pmatrix} V(k) \\ \text{given due to symmetry} \end{pmatrix}$$

NB here we are taking
The 2 band model
in principle, there is
an artificially large
mass!

$$\begin{aligned} \bar{G}_0 &= 0 \\ \bar{G}_1 &= \frac{2\pi}{a} \\ \bar{G}_2 &= \frac{4\pi}{a} \\ &\vdots \end{aligned}$$

Then is it is almost
constant \Rightarrow
Take only V_1 !

The only effect
I can have from a
periodic potential is
the removal of the
degeneracy at
zone boundary \rightarrow where
Bragg reflexions occur!

If the potential is small
I convix solutions
that are close in energy
 \Rightarrow zone boundary

Equivalent to say that
we approximate the
Bloch function with
the undisturbed plane
wave.

NB zone boundaries is
where Bragg reflexions
occur.

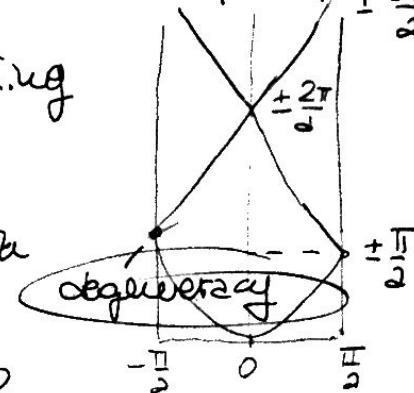
$$-b \pm \sqrt{b^2 - 4ac} \over 2a$$

This leads to the regular equation for the energy eigenvalues

$$\det \left[\left(\frac{\hbar^2 (k + G_n)^2}{2m} - \epsilon \right) \delta_{nn} + V(G_m - G_n) \right] = 0.$$

so far we did not make any assumption on the potential. Let's now consider a vanishingly small V and solve the regular equation for some specific cases:

Let's take $k = \frac{\pi}{a}$ \Rightarrow the interacting plane waves are characterized by wave numbers $\pm \frac{\pi}{a}$ with energy $E_0 = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2, \frac{\hbar^2}{2m} \left(\frac{3\pi}{a}\right)^2$, with degeneracy...



If the periodic potential is small we can focus our attention on the two basis functions

$$\psi_1(x) = \frac{1}{\sqrt{L}} e^{i\frac{\pi}{2}x}, \quad \psi_2(x) = \frac{1}{\sqrt{L}} e^{-i\frac{\pi}{2}x} \quad (\text{degenerate on the empty lattice})$$

regular equation becomes a 2×2 problem:

$$\det \begin{pmatrix} E_0 - \epsilon & V_1 \\ V_1^* & E_0 - \epsilon \end{pmatrix} = 0 \quad \text{where}$$

$V_1 = V \left(\frac{2\pi}{a}\right)$ \equiv F.T. of the potential corresponding to the first reciprocal lattice vector.

The periodic potential splits the energy levels:

$$\epsilon = E_0 \pm |V_1|^* \quad \text{The split is proportional to the Fourier component of the potential.}$$

This reasoning applies to other degenerate points of the Brillouin zone, $k=0, k=\pm\frac{\pi}{a} \Rightarrow$ energy bands separated by energy gaps.

What happens in the vicinity of the zone boundary point?

Let's take $k = \frac{\pi}{a} - \Delta k \Rightarrow$ the basis functions become \rightarrow

$$\psi_1(x) = \frac{1}{\sqrt{L}} e^{i(\frac{\pi}{2} + \Delta k)x}, \quad \epsilon_1 = \frac{\hbar^2}{2m} \left(\frac{\pi}{2} + \Delta k\right)^2 \text{ and}$$

$$\psi_2(x) = \frac{1}{\sqrt{L}} e^{-i(\frac{\pi}{2} + \Delta k)x}, \quad \epsilon_2 = \frac{\hbar^2}{2m} \left(\frac{\pi}{2} + \Delta k\right)^2.$$

Again we construct the 2×2 secular equation

$$\begin{vmatrix} \epsilon_1 - \epsilon & V_1 \\ V_1^* & \epsilon_2 - \epsilon \end{vmatrix} = 0 \quad \text{that has 2 solutions}$$

$$\epsilon = \frac{1}{2} (\epsilon_1 + \epsilon_2 \pm \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|V_1|^2}) \quad \text{that becomes,}$$

inserting the values for ϵ_1 and ϵ_2 :

$$\epsilon(\Delta k) = \epsilon_0 + \frac{\hbar^2(\Delta k)^2}{2m} \pm \frac{1}{2} \sqrt{16\epsilon_0 \frac{\hbar^2(\Delta k)^2}{2m} + 4|V_1|^2}.$$

If Δk is small \rightarrow Taylor series of the $\sqrt{\cdot}$:

$$\epsilon(\Delta k) = \epsilon_0 + \frac{\hbar^2(\Delta k)^2}{2m} \pm |V_1| \left[1 + \frac{2\epsilon_0}{|V_1|^2} \frac{\hbar^2(\Delta k)^2}{2m} + \dots \right].$$

Generalize To 3-dim

Again, we focus on points in the BZ where $\epsilon_n(\vec{k})$ is degenerate and see if a small periodic potential can ~~possibly~~ break the degeneracy \rightarrow perturbation theory.

$V(\vec{r})$ has the periodicity of the lattice

$$V(\vec{r}) = \sum_{m \neq 0} V(\vec{G}_m) e^{i\vec{G}_m \cdot \vec{r}} \quad \begin{matrix} (m=0 \text{ is the} \\ \text{mean value that} \\ \text{can be chosen} \\ \text{to be } \phi) \end{matrix}$$

At the same time, we can do it for the Bloch function

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \sum_m \underbrace{U(\vec{G}_m)}_{U(\vec{k}, \vec{r})} e^{i\vec{G}_m \cdot \vec{r}} \quad \begin{matrix} (m=0 \text{ is} \\ \text{the free} \\ \text{plane wave} \\ \text{solution}) \end{matrix}$$

If the potential is weak, the terms for $m \neq 0$ are weak (small perturbation on the free el. wave function) \Rightarrow consider only $U(0)$, and $U(\vec{G}_m) \ll U(0)$.

The full Schrödinger eq. (with no approx) becomes

$$\frac{1}{\sqrt{V}} \sum_m \left[\frac{\hbar^2}{2m} (\vec{k} + \vec{G}_m)^2 - \epsilon(\vec{k}) + \sum_e V(\vec{G}_e) e^{i\vec{G}_e \cdot \vec{r}} \right] U(\vec{G}_m) e^{i(\vec{k} + \vec{G}_m) \cdot \vec{r}} = 0$$

or else, the secular equation:

$$\nabla \left(\frac{\hbar^2}{2m} (\vec{k} + \vec{G}_n)^2 - \epsilon(\vec{k}) \right) u(\vec{G}_n) + \sum_m V(\vec{G}_n - \vec{G}_m) u(\vec{G}_m) = 0$$

First approximation:

1. Take $\epsilon(\vec{k})$ to be $\frac{\hbar^2 k^2}{2m} \Rightarrow$

$$u(\vec{G}_n) \approx \frac{V(\vec{G}_n)}{\frac{\hbar}{2m} [(\vec{k} + \vec{G}_n)^2 - k^2]} . \quad \begin{array}{l} \text{In general, if} \\ V(\vec{G}_n) \text{ is small} \\ u(\vec{G}_n) \text{ is small} \end{array} \Rightarrow$$

small perturbation of the plane wave.

But, for $(\vec{k} + \vec{G})^2 - k^2 = 0 \quad [\text{Bragg reflexion}]$

$u(\vec{G}_n)$ are large $\Rightarrow u(0)$ and $u(\vec{G}_n)$ are of the same order and need to be considered.

This leads to the regular equations for $k^2 = (\vec{k} + \vec{G}_p)^2$

$$\left\{ \begin{array}{l} \left(\frac{\hbar^2}{2m} k^2 - \epsilon(\vec{k}) \right) u(0) + V(-\vec{G}_p) u(\vec{G}_p) = 0 \\ \left(\frac{\hbar^2}{2m} (\vec{k} + \vec{G}_p)^2 - \epsilon(\vec{k}) \right) u(\vec{G}_p) + V(\vec{G}_p) u(0) = 0 \end{array} \right.$$

solving for $\epsilon(\vec{k})$ gives $\epsilon = \frac{\hbar^2 k^2}{2m} \pm |V(\vec{G}_p)|$

$$[V(-\vec{G}_p) = V^*(\vec{G}_p)] .$$

For all \vec{k} vectors satisfying a Bragg condition, the energy splits with gap proportional to the Fourier component of the potential.

Note on the periodic potential

1. $V(\vec{r})$ can be made as the superposition of atomic potentials centered at the positions of the ions \rightarrow
what if we have a lattice with a basis: $BL + \text{basis}$

$$V(\vec{r}) = \sum_{\vec{R}} \sum_j \phi(\vec{r} - \vec{R} - \vec{j}_j) \quad \begin{matrix} \text{atomic} \\ \text{periodic} \\ \text{G vectors} \end{matrix}$$

↓
ionic positions
in the unit cell.

$$V(\vec{G}) = \frac{1}{V} \int_{\text{cell}} d\vec{r} e^{i\vec{G} \cdot \vec{r}} \sum_{\vec{R}, j} \phi(\vec{r} - \vec{R} - \vec{j}_j) = \frac{1}{V} \int_{\text{space}} d\vec{r} e^{i\vec{G} \cdot \vec{r}} \sum_j \phi(\vec{r} - \vec{j}_j) =$$

$$= \frac{1}{V} \phi(\vec{G}) S_{\vec{G}}^* \quad \text{where we define}$$

$$\phi(\vec{G}) = \int_{\text{space}} d\vec{r} e^{-i\vec{G} \cdot \vec{r}} \phi(\vec{r}) \quad \text{and}$$

$$S_{\vec{G}} = \sum_j e^{i\vec{G} \cdot \vec{j}_j} \equiv \underline{\text{structure factor}}$$

$V(\vec{G}) = 0$ either if $\phi(\vec{G}) = 0$ or, even if $\phi(\vec{G}) \neq 0$, if
 $S_{\vec{G}} = 0 \Rightarrow$ no band splitting.

Introduction to the pseudopotential method.

Use the fact that in many cases the periodic potential is indeed weak \rightarrow replace the total potential with an effective potential - empirically fitted to reproduce energy bands.

for a system ~~with~~ with a basis, the regular equation for the energies becomes:

$$\det \left[\left[\frac{\hbar^2}{2m} (\vec{k} + \vec{G}_n)^2 - \epsilon \right] S_{nn} + \sum_j e^{-i(\vec{G}_m - \vec{G}_n) \cdot \vec{r}_j} \underbrace{V_j(\vec{G}_m - \vec{G}_n)}_0 \right] = 0$$

$\begin{matrix} \text{atomic} \\ \text{pseudopotential} \\ \text{parameters} \end{matrix} \quad \downarrow$

④ M.L. Cohen, T.K. Bergmaner, Phys. Rev. 141, 789 (1966)

I project

Tight binding

This will describe
only an approximate
energy eigenstate.

However, the best estimate
of the lower energy eigenvalue
can be obtained by minimizing
the entire expression

Set the partial
derivatives with respect
to u_1 and u_2^* to zero

2 atomic orbitals

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{u_1^* u_1 \langle 1 | H | 1 \rangle + u_1^* u_2 \langle 1 | H | 2 \rangle + u_2^* u_1 \langle 2 | H | 1 \rangle + u_2^* u_2 \langle 2 | H | 2 \rangle}{u_1^* u_1 + u_2^* u_2}$$

$$\begin{aligned} \frac{dE}{du_1^*} = 0 \Leftrightarrow & \frac{u_1^* H_{11}}{u_1^* u_1 + u_2^* u_2} - \frac{u_1^* u_1 H_{11} u_1}{(u_1^* u_1 + u_2^* u_2)^2} + \frac{u_2^* H_{12}}{u_1^* u_1 + u_2^* u_2} - \frac{u_1^* u_2 \langle 1 | H | 2 \rangle}{(u_1^* u_1 + u_2^* u_2)^2} u_1 \\ & - \frac{u_2^* u_1 \langle 2 | H | 1 \rangle}{(u_1^* u_1 + u_2^* u_2)^2} u_1 - \frac{u_2^* u_2 \langle 2 | H | 2 \rangle}{(u_1^* u_1 + u_2^* u_2)^2} u_1 \end{aligned}$$

The Tight binding method

Different perspective \rightarrow consider a solid as a superposition of atoms, each with their electronic states \rightarrow states are close enough so that the electronic wavefunctions overlap \rightarrow The energy of the states will change but the number of states will be the same

Energy of electronic states in molecules or solid can be approximated by a linear combination of atomic orbitals, LCAO.

\hookrightarrow we use atomic orbital as a basis for the expansion of the electronic wavefunctions (like p-orbitals in the weak potential approx.)

1. enumerate each of the electronic states of the atom that will be used in the mathematical expansion for the states of the molecule/solid

$$|\Psi\rangle = \sum_{\alpha} u_{\alpha} |\alpha\rangle$$

coefficients to be determined \hookrightarrow atomic orbitals chosen to be orthogonal:

$$\langle \alpha | \alpha \rangle = 1 ; \langle \alpha | \beta \rangle = 0$$

The u_{α} can be found by imposing the condition of the energy of the state:

$$E = \min \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \text{ will be minimum, or equivalently,}$$

$$-\delta \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \delta \frac{\sum_{\alpha} u_{\alpha}^* u_{\alpha} \langle \beta | H | \alpha \rangle}{\sum_{\alpha} u_{\alpha}^* u_{\alpha}} = 0, \text{ That is equivalent to}$$

$$\boxed{\sum_{\alpha} \langle \beta | H | \alpha \rangle u_{\alpha} - E u_{\beta} = 0}$$

~~negative of the derivative of the total energy with respect to u_{β} is zero.~~

Considering a particular u_{β}^* , the above expression can be written as

$$\frac{\sum_{\alpha} u_{\alpha} \langle \beta | H | \alpha \rangle}{\sum_{\alpha} u_{\alpha}^* u_{\alpha}} - \frac{\sum_{\alpha} u_{\alpha}^* u_{\alpha} \langle \beta' | H | \alpha \rangle u_{\beta}}{(\sum_{\alpha} u_{\alpha}^* u_{\alpha})^2} = 0 \text{ for each } u_{\beta}.$$

This is equivalent to

$$\boxed{\sum_{\alpha} \langle \beta | H | \alpha \rangle u_{\alpha} - E u_{\beta} = 0}.$$

This is (again) a linear system of equations for the coefficients = eigenvalue problem

↳ There are as many eigenvalues E as many basis functions we consider and the lower energy corresponds to the lower energy state for the electron.

The energies can be obtained directly solving (yet again) a secular equation

$$\det \left\| H_{\beta\alpha} - E \delta_{\beta\alpha} \right\| = 0$$

Example: The H_2 molecule



$\Psi = \Psi_1 |1\rangle + \Psi_2 |2\rangle$ and solve the secular equation

$$\begin{vmatrix} H_{11} - E & -V_{SSS} \\ -V_{SSS} & H_{22} - E \end{vmatrix} = 0$$

Here $H_{11} = H_{22} = E_S$
and

$$-V_{SSS} = H_{12} = H_{21}$$

The solution of the secular equation is trivial:

$$E = E_S \pm V_{SSS}$$

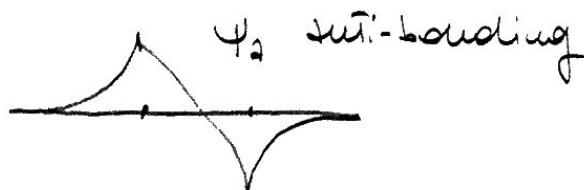
E_s : $E_a = E_S + V_{SSS}$

The eigenvectors Ψ_1 and Ψ_2 can be trivially obtained by solving the equations given above

$$\Psi_1 = \Psi_2 = \frac{1}{\sqrt{2}} \Rightarrow \Psi_b = \frac{1}{\sqrt{2}} |1\rangle + \frac{1}{\sqrt{2}} |2\rangle$$



$$\Psi_a = \frac{1}{\sqrt{2}} |1\rangle - \frac{1}{\sqrt{2}} |2\rangle$$



→ extension to a periodic system: 1 dim crystal made by equal atoms at positions $t_n = n a$ (lattice points).

Each atom has a local orbital ϕ_k of energy E_k , and the total number of atoms in the chain is N .

We want to obtain the crystal wave function as a series in the basis of the atomic orbital functions $\phi_\alpha(x - t_n)$ each centered at the atomic site t_n .

It is convenient to express the crystal Hamiltonian H in the atomic basis and exploit only the translational symmetry of the system.

1. Since the system is translationally symmetric (see the sites are the same)

**TIGHT
BINDING**

$$\langle \phi_\alpha(x - t_n) | H | \phi_\alpha(x - t_n) \rangle = H_{nn} = E_0$$

are all the same.

2. Assuming that the relevant interaction is between nearest neighbors. The only relevant elements are of the form

$$\langle \phi_\alpha(x - t_n) | H | \phi_\alpha(x - t_{n\pm 1}) \rangle = H_{n,n\pm 1} = \gamma$$

They are also all the same for the translational invariance. γ = interaction energy is taken to be negative (stable bonding).

The atomic orbitals $\phi_\alpha(x - t_n)$ do not satisfy Bloch's theorem, but a linear combination of them (LCAO) does:

$$\Phi(k, x) = \frac{1}{\sqrt{N}} \sum_n e^{ikt_n} \phi_\alpha(x - t_n) \equiv \text{Bloch sum}$$

In fact

$$\begin{aligned} \Phi(k, x + t_m) &= \frac{1}{\sqrt{N}} \sum_n e^{ikt_n} \phi_\alpha(x + t_m - t_n) = \\ &= e^{ikt_m} \frac{1}{\sqrt{N}} \sum_n e^{ik(t_n - t_m)} \phi_\alpha(x - t_n + t_m) = \\ &= e^{ikt_m} \Phi(k, x) \end{aligned}$$

Note: a Bloch sum spans the same Hilbert space of the localized atomic functions — but \rightarrow Bloch sums of different k do not mix under any periodic forcefield.

The energy bands that arise from the N atomic orbitals are thus given by

$$E(k) = \langle \Phi(k, x) | H | \Phi(k, x) \rangle$$

which gives, given the previous hypothesis

$$E(k) = E_0 + 2\gamma \cos ka$$

$\epsilon = \epsilon_0 + 2\gamma \cos k \approx \epsilon_0 + 2\gamma - \gamma^2 k^2 \rightarrow$
 for small k This is again a
 similar to the free electron case \rightarrow parabolic form,
 can be written

$$\epsilon(k) \approx \frac{\hbar^2 k^2}{2m^*}, \text{ where } m^* = \frac{\hbar^2}{2|\gamma|a^2} = \text{effective mass}$$

renormalization of the electron mass due to the periodic potential [once again!].

Note: The TB Hamiltonian is Tridiagonal and can be written in the form:

$$H = \epsilon_0 \sum_n |f_n\rangle \langle n| + \gamma \sum_n [n\rangle \langle n+1| + |n+1\rangle \langle n|]$$

$$|n\rangle = \phi_n(x-t_n).$$

Extension to more realistic crystalline systems The Tight Binding method.

1. 3dim crystal with one atom per unit cell: The diatomic is just an extension (Tridiag) of the 1dim case.

$\phi_i(\vec{r}) \rightarrow$ atomic orbitals of energy E_i , where i is the quantum number of the orbital (s, p, d etc).

The 3dim Bloch sum becomes

~~for Bloch function~~
$$\Phi_i(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{R_m} e^{i\vec{k} \cdot \vec{R}_m} \phi_i(\vec{r} - \vec{R}_m)$$

number of cells \rightarrow $\vec{R}_m \equiv \vec{R}_{m1} \equiv \vec{R}_{m2} \equiv \dots \equiv \vec{R}_{mN} \equiv \vec{R}_m$ vectors of the crystal.

In TB the full crystal wavefunction is constructed as a linear combination of Bloch sums of wave vector \vec{k} :

$$\Psi(\vec{k}, \vec{r}) = \sum_i c_i(\vec{k}) \Phi_i(\vec{k}, \vec{r})$$

This leads to the secular equation

$$\det \left\| M_{ij}(\vec{k}) - \epsilon S_{ij}(\vec{k}) \right\| = 0 \quad \text{where}$$

M_{ij} = matrix elements of the crystal H between Bloch sums

S_{ij} = overlap matrix elements

$$H_{ij}(\vec{k}) = \langle \Phi_i(\vec{k}, \vec{r}) | H | \Phi_j(\vec{k}, \vec{r}) \rangle$$

$$S_{ij}(\vec{k}) = \langle \Phi_i(\vec{k}, \vec{r}) | \Phi_j(\vec{k}, \vec{r}) \rangle.$$

Typically these matrix elements can be either computed by the knowledge of the crystal Hamiltonian, but most often they are obtained in a semiempirical way:

- Assuming that the orbitals are sufficiently localized. The overlap between neighboring atoms are negligible \Rightarrow localized atomic orbitals are orthogonal $S_{ij} = I_{ij}$ identity ($S = I$).

- Express the crystal potential as a superposition of spherically symmetric potentials (atomic-like) centered at the lattice positions:

$$H_{ij}(\vec{k}) = \frac{1}{N} \sum_{mn} e^{i\vec{k} \cdot (\vec{R}_m - \vec{R}_n)} \langle \Phi_i(\vec{r} - \vec{R}_m) | H | \Phi_j(\vec{r} - \vec{R}_n) \rangle$$

with $H = \frac{p^2}{2m} + \sum_{\vec{R}_n} V_n(\vec{r} - \vec{R}_n)$.

Combining the two expressions above one is left with the problem of determining integrals of the form

$$I_{ij}(R_I) = \int \Phi_i^*(\vec{r}) V_n(\vec{r} - \vec{R}_I) \Phi_j(\vec{r} - \vec{R}_I) d\vec{r}$$

where \vec{R}_I spans all the ^{up to} nearest neighbors.

In this way $H_{ij}(\vec{k}) = E_i S_{ij} + \sum_{\vec{R}} I_{ij}(R_I) e^{i R_I \vec{k}}$

$R_I = 0$	$I_{ij} \equiv$ crystal field integral	\Rightarrow constant \Rightarrow neglected
$R_I \neq 0$	$I_{ij} \equiv$ two center integrals	

$$I_{ss} = V_{SS\sigma}$$

$$I_{pp\sigma} = e_x^2 V_{PP\sigma} + (1 - e_x^2) V_{PP\pi}$$

$$I_{sp_x} = e_x V_{SP\sigma}$$

$$I_{pp\gamma} = e_x e_y [V_{PP\sigma} - V_{PP\pi}]$$

e_x, e_y, e_z = direction cosines
of the two center distance

and all others

by cyclic permutations.

$$I_{pp\delta} = e_x e_z [V_{PP\sigma} - V_{PP\pi}]$$

One electron approximations and Hartree-Fock

From The many body Hamiltonian \rightarrow Born-Oppenheimer

$$\rightarrow H_e = \sum_{i=1}^N h(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{r_{ij}}, \quad h(F) = \frac{\vec{P}^2}{2m} + V_{\text{ext}}(\vec{r})$$

↓

solutions of $H_e \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \xi_1, \xi_2) = E \Psi(\xi_1, \xi_2, \dots, \xi_N)$

(1) uniform non interacting electron gas \rightarrow see
green notebook (Drude) \rightarrow see later for Jellium!

(2) Hartree equations

$\Psi(\xi_1, \xi_2, \dots, \xi_N)$ \rightarrow combination of 1-electron orbitals:

$$\psi_i(\vec{r}, \xi) = \phi_i(\vec{r}) \chi_i(\xi)$$

invariant
orbital spin

Hartree: $\Psi(\xi_1, \xi_2, \dots, \xi_N) = \psi_1(\vec{r}_1, \xi_1) \cdot \psi_2(\vec{r}_2, \xi_2) \cdot \dots \cdot \psi_N(\vec{r}_N, \xi_N)$

↙ Ansatz for the many-body wavefunction

NOTE: not correct antisymmetry character (Pauli)
 \rightarrow need to be considered ad-hoc

With this ansatz, the electron density becomes

$$\rho(\vec{r}) = (-e) \sum_{i=1}^{(\text{occ})} \phi_i^*(\vec{r}) \phi_i(\vec{r})$$

and the Coulomb potential associated to this density is

$$V_{\text{Coulomb}}(\vec{r}) = \sum_{j=1}^{(\text{occ})} \int \phi_j^*(\vec{r}') \frac{e^2}{|\vec{r} - \vec{r}'|} \phi_j(\vec{r}') d\vec{r}'$$

Each electron moves in the effective field generated by all other $N-1$ electrons

Equivalent to the classical electrostatic energy of a given charge distribution

(3) Determinantal wavefunction

Starting from a set of orthogonal 1-electron wavefunctions one can force directly the antisymmetry and construct a Ψ that automatically respects the Pauli principle

Slater determinants: $\Psi_0(\xi \dots \xi) = \frac{1}{\sqrt{N!}} \det (\psi_1 \psi_2 \psi_3 \dots \psi_N)$

or

$$\Psi_0(\xi \dots \xi) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1, \xi_1) & \psi_1(r_2, \xi_2) & \dots \\ \psi_2(r_1, \xi_1) & \psi_2(r_2, \xi_2) & \dots \\ \vdots & \vdots & \ddots \end{vmatrix}$$

NB $\det A = 0$ if
Two rows or
columns are the
same \equiv electrons
occupy the same
state.

With determinantal wavefunctions Hamiltonian
matrix elements take a particularly interesting form:
He contains / 1-particle operators (\hat{h}_i) at r_i
2-particle operators (\hat{c}_{ij}) —

$$- G_1 = \sum_{i=1}^N h(r_i)$$

$$- G_2 = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

IT can be easily determined
that

$$\langle \Psi_0 | G_1 | \Psi_0 \rangle = \bar{\zeta} \langle \psi_i | h | \psi_i \rangle \text{ and}$$

$$\langle \Psi_0 | G_2 | \Psi_0 \rangle = \frac{1}{2} \bar{\zeta} \left[\underbrace{\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle}_{\text{coupons integral} = Q_{ij}} - \underbrace{\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle}_{\text{exchange integral} = T_{ij}} \right]$$

Q_{ij} : by direct integration of the spins $\Rightarrow Q_{ij}$ does not
depend ~~especially~~ on the spin part:

$$Q_{mn} = \langle \psi_m \psi_n | \frac{e^2}{r_{12}} | \psi_m \psi_n \rangle = \int \phi_m^*(\vec{r}_1) \phi_m^*(\vec{r}_2) \frac{e^2}{r_{12}} \phi_m(\vec{r}_1) \phi_m(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

\equiv interaction between two classical
charge densities: $-e |\phi_m(\vec{r}_1)|^2$ and
 $-e |\phi_m(\vec{r}_2)|^2 \rightarrow$ long range interaction

$$T_{mn} = \langle \psi_m \psi_n | \frac{e^2}{r_{12}} | \psi_n \psi_m \rangle = \delta_{mn} \cdot \int \phi_m^*(\vec{r}_1) \phi_n^*(\vec{r}_2) \frac{e^2}{r_{12}} \phi_n(\vec{r}_1) \phi_m(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

- different from zero only for parallel spins
- short ranged if ϕ_n strongly localized

~~Wannier states are not orthogonal~~

④ Hartree-Fock equations

Expectation value of the electronic hamiltonian for determinantal wave functions:

$$E_0 = \sum_i \langle \psi_i | h | \psi_i \rangle + \frac{1}{2} \sum_{ij} \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]$$

This must be minimized w.r.t. $E_0 = E_0(\{\psi_i\}) = \text{min}$.
→ Variational principle under the orthonormality constraint $\langle \psi_i | \psi_j \rangle = \delta_{ij}$
↓ The minimization of the functional leads to the Hartree-Fock equations

$$\left[\frac{P^2}{2m} + V_{\text{coul}}(\vec{r}) + V_H(\vec{r}) + V_{\text{exch}}(\vec{r}) \right] \psi_i = \sum_j \epsilon_{ij} \psi_j$$

where

$$V_H \psi_i(\vec{r}) = \sum_j^{\infty} \psi_i(\vec{r}) \int \psi_j(\vec{r}_2) \frac{e^2}{|\vec{r}-\vec{r}_2|} \psi_j(\vec{r}_2) d\vec{r}_2$$

and

$$V_{\text{exch}} \psi_i(\vec{r}) = - \sum_j^{\infty} \psi_i(\vec{r}) \int \psi_j(\vec{r}_2) \frac{e^2}{|\vec{r}-\vec{r}_2|} \psi_i(\vec{r}_2) d\vec{r}_2$$

standard Hartree potential

↳ integral operator

Note

Exchange energy is negative \Rightarrow lower energy = more stable \rightarrow concept of exchange hole

correlation \Rightarrow all the rest!

⑤ Homogeneous electron gas: interaction of electrons in a uniform background of positive charge

0th order

uniform non-interacting electron gas \rightarrow Drude

fⁿ order

interaction at the Hartree-Fock level

Jellium model

$$E(k) = \frac{\hbar^2 k^2}{2m} \quad \text{and} \quad \Psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \cdot \text{plane waves.}$$

Note in The Jellium model V_{exch} (positive background) cancels The Hartree potential (negative background)!!!

$$H_e = \frac{P^2}{2m} + V_{\text{exch}}$$

disappear
in
the plane wave
basis

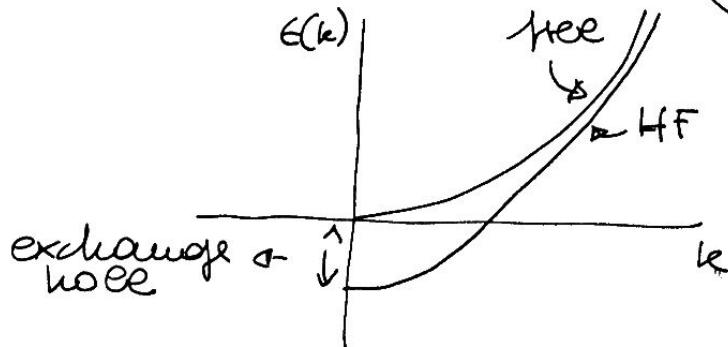
also disappear in
the basis of plane
waves

$$V_{\text{exch}} e^{i\vec{k}\cdot\vec{r}} = -e^{\vec{k}\cdot\vec{r}} \frac{1}{\sqrt{qck_F}} \sum_{\vec{q}} \frac{4\pi e^2}{|k-\vec{q}|} =$$

$$= -\frac{2e^2 k_F}{\pi} \left(\frac{k}{k_F} \right) e^{i\vec{k}\cdot\vec{r}} \quad \text{and}$$

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|. \quad \text{from here comes the eigenvalue } \epsilon_i:$$

$$\epsilon_i = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right).$$



If we take the average value of $F(x)$: $\langle F(x) \rangle = \frac{3}{4} \Rightarrow$

$$V_{\text{exch}} = -\frac{3}{2} \frac{e^2}{\pi} k_F = -\frac{3}{2} \frac{e^2}{\pi} [3\pi^2 n]^{1/3}.$$

assuming a slowly varying $n(\vec{r}) \rightarrow$

$$V_{\text{exch}}(\vec{r}) = -\frac{3}{2} \frac{e^2}{\pi} [3\pi^2 n(\vec{r})]^{1/3}$$

Density Functional Theory

From many-body electron wavefunction to one-body electron density

Consider the electron Hamiltonian H_e as

$$H_e = H_{int} + V_{ext} \quad \text{where}$$

$$H_{int} = \underset{\text{interact.}}{\underset{\text{cont.}}{T + V_{ee}}} = \sum_i \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

and

$$V_{ext} = \sum_i V_{ext}(\vec{r}_i) \quad \text{and}$$

$$V_{ext}(\vec{r}) = V_{\text{ext.}}(F) = - \sum_I \frac{Z_I e^2}{|F - \vec{R}_I|}.$$

Let's consider a non-degenerate ground state and consider n as variable of the many-electron problem. The external potential $V_{ext}(\vec{r})$ - all the rest (imperfections, etc.) fixed.

Floerchinger-Kohn Theorem

1-to-1 correspondence between the ground state density of a N -electron system and the external potential acting on it.

knowledge of $V_{ext}(\vec{r}) \Rightarrow \Psi_G[V_{ext}] \Rightarrow n(F)$ where

$$n(F) = \langle \Psi_G \{ \vec{r}_i \} | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi_G \{ \vec{r}_i \} \rangle$$

This can be summarized by saying that there exists a functional F which gives $n(F)$ such V_{ext} and we write this as

$$n(F) = F[V_{ext}]$$

The novelty of Theorem is that this relation can be inverted so that

$$V_{ext} = G[n(F)] \quad \text{The external}$$

potential is a functional of the density, and from the knowledge of $n(F)$ we can determine uniquely $V_{ext}(F)$.

[see demonstration on slides]

Hohenberg-Kohn theorems

- Proofs of H-K theorems are exceedingly simple and just based on a single reduction ad absurdum argument
- Proof of Theorem 1: suppose there were two different exchange potentials V and V' with same ground state energy, etc.
- The two potentials lead to two different contributions with different contributions. They are proportional to each other since $\delta E = \delta E_1 + \delta E_2$

$$E = E(V) - E(V') = (\delta E_1 + \delta E_2) \propto \delta E$$

which contradicts

$$E = E(V) - E(V') = (\delta E_1 + \delta E_2) \propto \delta E$$

So changing the potential we change the

$$E = E(V) - E(V')$$

Therefore the above contradiction we get the desired result

$$\delta E = \delta E_1 + \delta E_2$$

As for the density, we can define other obvious functionals of the external potential:

$$V_{\text{ext}} \rightarrow \Phi_{\text{e}}[V_{\text{ext}}] \left\{ \begin{array}{l} \Rightarrow E[V_{\text{ext}}] \\ \Rightarrow T[V_{\text{ext}}] \\ \Rightarrow V_{\text{ee}}[V_{\text{ext}}] \end{array} \right.$$

because of the H-K Theorem V_{ext} and n are in a 1-to-1 correspondence. The above quantities can be expressed equivalently as functionals of the density

$$\left\{ \begin{array}{ll} \text{ground-state energy, } & E[n(\vec{r})] \\ \text{kinetic energy, } & T[n(\vec{r})] \\ \text{exp. value of } V_{\text{ee}}, & V_{\text{ee}}[n(\vec{r})]. \end{array} \right.$$

~~Because~~ of the H-K Theorem gives us a variational principle for the ground-state density! →

$$E^{\text{HK}}[n(\vec{r}), V_{\text{ext}}(\vec{r})] = T[n(\vec{r})] + V_{\text{ee}}[n(\vec{r})] + \int V_{\text{ext}} n(\vec{r}) d\vec{r}$$

E^{HK} is minimal at the ground-state density ⇒ ground-state energy

Note → The functional $T[n] + V_{\text{ee}}[n]$ is universal, i.e. does not depend on V_{ext} .
However, it is NOT known!!

↓
Kohn-Sham equations → obtained through the minimization of the HK functional, taking for $n(\vec{r})$ the form

$$n(\vec{r}) = \sum_i \phi_i^*(\vec{r}) \phi_i(\vec{r}) \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

and ϕ_i chosen as orbitals of an independent electron system - Kohn-Sham ansatz:

formulate the existence of a non-interacting electron system whose density $n^0(\vec{r}) \equiv n(\vec{r})$

↳ Advantage: kinetic energy of a non-interacting system

$$T_0[n] = \sum_i \left\langle \phi_i \left| -\frac{\hbar^2 \nabla^2}{2m} \right| \phi_i \right\rangle \quad \text{and}$$

Hartree potential

$$V_H[n] = \frac{1}{2} \sum_{i,j} \langle \phi_i \phi_j | \frac{e^2}{r_{ij}} | \phi_i \phi_j \rangle = \frac{1}{2} \int n(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}'|} n(\vec{r}') d\vec{r} d\vec{r}'$$

so that

$$E_{HK}[u] = T_0[u] + V_H[u] + \int v_{\text{ext}}(\vec{r}) u(\vec{r}) d\vec{r} + E_{xc}[u]$$

$$E_{xc} = T[u] - T_0[u] + V_{ee}[u] - V_H[u]$$

↳ The big unknown \rightarrow to be approximated!