

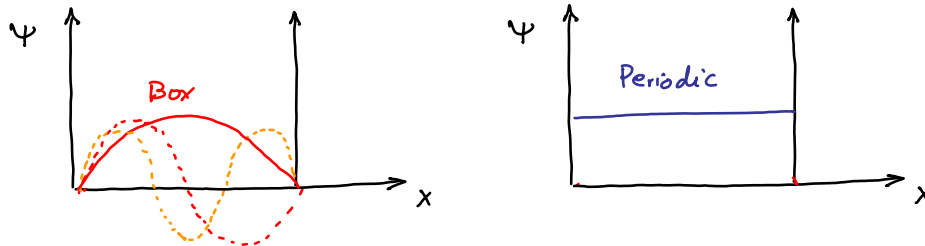
## Session 9

Note Title

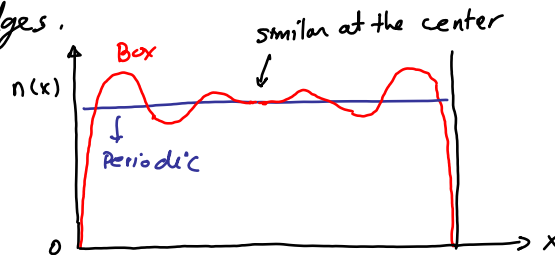
10/9/2008

### Example Particle in a box or ring

Consider the wave functions of the periodic (ring) and infinite well boundary (Box) boundary condition:



The electron density  $n(x) = |\Psi(x)|^2$  for both cases is identical at the center but differ at the edges.



In large systems, boundary conditions can be ignored. Since the difference happens close to the ends, we can safely mostly use periodic boundary condition.

Recal electron density is given by:

$$n(x) = \sum_{\alpha} |\Phi_{\alpha}(x)|^2 f_{\alpha}$$

$$f_0(\epsilon_{\alpha} - \mu) = \frac{1}{1 + e^{\frac{\epsilon_{\alpha} - \mu}{k_B T}}}$$

$n(x)$  can be viewed as diagonal elements of a much more general concept, i.e.

the equilibrium density matrix:

$$[\rho] = f_0([H] - \mu[I])$$

$[\rho]$  can be written in any basis or "space" such as in 3D real or momentum space.

But in **any space** the diagonal elements of  $[\rho]$  will always be the electron density.

Another common expression for the density matrix in real space is:

$$\rho(x, x') = \sum_{\alpha} \phi_{\alpha}(x) f_{\alpha} (\epsilon_{\alpha} - \mu) \phi_{\alpha}^*(x')$$

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We know that for a given wavefunction  $\phi_{\alpha}$ ,  $|\phi_{\alpha}|^2$  is the probability distribution function.

Let's assume that we can write the wavefunction of a system as:

$$\psi = \sum_{\alpha} \phi_{\alpha}(x) \sqrt{f_{\alpha}}$$

$$\begin{aligned} \Rightarrow \rho &= \psi^* \psi = \sum_{\alpha} \sum_{\beta} \phi_{\alpha}^*(x) \phi_{\beta}(x) f_{\alpha} \\ &= \sum_{\alpha} |\phi_{\alpha}|^2 f_{\alpha} + \underbrace{\sum_{\alpha} \sum_{\beta \neq \alpha} \phi_{\alpha}^*(x) \phi_{\beta}(x) f_{\alpha}} \end{aligned}$$

to get rid of this term let's define  $\psi$  a bit different.

$$\psi = \sum_{\alpha} \phi_{\alpha}(x) C_{\alpha}$$

and define  $C_{\alpha}$ 's as:

$$\left. \begin{aligned} C_{\alpha} C_{\beta}^* &= |C_{\alpha}|^2 = f_{\alpha} & \alpha = \beta \\ C_{\alpha} C_{\beta}^* &= 0 & \alpha \neq \beta \end{aligned} \right\} \text{or: } C_{\alpha} C_{\beta}^* = f_{\alpha} \delta_{\alpha\beta}$$

In this way  $C_{\alpha} C_{\beta}^*$  is indeed the density matrix in the eigenstate basis:

$$\rho_{\alpha\beta} = f_{\alpha} \delta_{\alpha\beta}$$

$$\Rightarrow \boxed{\psi(x) = \sum_{\alpha} \phi_{\alpha}(x) \sqrt{f_{\alpha}}}$$

---

$\rho_{\alpha\beta}$  is diagonal only in eigenstate basis. Why?

Let's look at sch. equ - to answer this question:

$$i\hbar \frac{\partial \Psi}{\partial t} = H_{op} \Psi \quad \text{in eigenstate basis we have:}$$

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \end{bmatrix} = \begin{bmatrix} \epsilon_1 & & & \\ & \epsilon_2 & & \\ & & \ddots & \\ & & & \epsilon_n \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \end{bmatrix}$$

which is basically  $n$  linearly independent differential equations:

$$i\hbar \frac{\partial}{\partial t} \psi_1 = \epsilon_1 \psi_1$$

$$i\hbar \frac{\partial}{\partial t} \psi_2 = \epsilon_2 \psi_2$$

$\vdots$

$$\text{and } \psi_j(t) = \psi_j(0) e^{-i\epsilon_j t/\hbar}$$

So there is no overlap between members of eigenstate basis; so the Hamiltonian must be diagonal.

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- Main point

- Fermi distribution was used to write  $\rho$  in eigenstate basis.

$$\rho = f([H]) - \mu [I]$$

$$\rho_{\alpha\beta} = f_{\alpha} \delta_{\alpha\beta}$$

- Most properties of a material can be calculated from the density matrix.

Example

Calculate the current  $I$  using the density matrix.

$$I = env$$

↓      ↘  
electron density    electron velocity

$n$  is given from the density matrix. So we only need to calculate  $v$ . For that, we must develop a velocity operator,  $v_{op}$ . The expectation value to velocity is then:

$$\langle v \rangle = \int d\vec{r} \Psi^* v_{op} \Psi$$

Momentum operator is:  $P_{op} = -i\hbar \frac{\partial}{\partial x}$  in 1D.

in general:  $\vec{P}_{op} = -i\hbar \vec{\nabla}$

So velocity would be:  $\vec{V}_{op} = -\frac{i\hbar}{m} \vec{\nabla}$  Let's expand  $\langle v \rangle$  now:

$$\langle v \rangle = \int d\vec{r} \sum_{\alpha} \phi_{\alpha}^*(\vec{r}) C_{\alpha}^* V_{op} \sum_{\beta} \phi_{\beta}(\vec{r}) C_{\beta}$$

$$= \sum_{\alpha} \sum_{\beta} C_{\alpha}^* C_{\beta} \int d\vec{r} \phi_{\alpha}^*(\vec{r}) V_{op} \phi_{\beta}(\vec{r})$$

$\rho_{\alpha\beta}$   $\equiv V_{\alpha\beta}$  (this how we always define a matrix element)

$$\downarrow$$

$$A_{\alpha\beta} = \int d\vec{r} \phi_{\alpha}^* A_{op} \phi_{\beta}$$

$$= \sum_{\alpha} \sum_{\beta} V_{\alpha\beta} \rho_{\alpha\beta} = \sum_{\alpha} V_{\alpha\alpha} \rho_{\alpha\alpha} = \sum_{\alpha} [V\rho]_{\alpha\alpha}$$

$$= \text{Trace}(V)$$

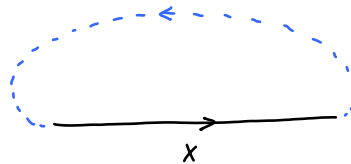
velocity matrix      density operator

$$\Rightarrow \boxed{\langle v \rangle = \text{Trace}(V\rho)}$$

Box with periodic boundary condition:

This box is like a ring:

the eigenvectors are:  $e^{ikx}$  and  $e^{-ikx}$ .



Intuitively  $e^{+ikx}$  passes positive momentum and carry current in the +x direction.

And  $e^{-ikx}$  in the -x direction. So the velocity matrix is:

$$V = \begin{bmatrix} \frac{\hbar k}{m} & 0 \\ 0 & -\frac{\hbar k}{m} \end{bmatrix} \quad \text{where } P_{op} = -i\hbar \frac{\partial}{\partial x}$$

Given two electrons at equilibrium, each state is equally occupied:

$$\rho = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

If we now apply a positive voltage to the terminal at +x end, stats move such that there is more current to +x direction. Say for example:

$$\rho = \begin{bmatrix} 1.5 & 0 \\ 0 & 0.5 \end{bmatrix}$$

This is intuitively understandable.

However, interpreting  $\rho$  when working in another basis is difficult.

Suppose instead of  $e^{\pm ikx}$ , we use  $\cos kx$  and  $\sin kx$ . In this case the velocity

matrix is:

$$v = \frac{i\hbar}{m} \begin{bmatrix} \int_0^L \cos kx \frac{\partial}{\partial x} \cos kx & \int_0^L \sin kx \frac{\partial}{\partial x} \cos kx \\ \int_0^L \cos kx \frac{\partial}{\partial x} \sin kx & \int_0^L \sin kx \frac{\partial}{\partial x} \sin kx \end{bmatrix}$$

$$= \begin{bmatrix} 0 & i\hbar k / 2mL \\ i\hbar k / 2mL & 0 \end{bmatrix} \quad \text{where } k = \frac{2n\pi}{L}$$

Now in this basis, since we have off diagonal terms, it is not clear what the eigenvalues are. The situation is more complex for large systems.

For this reason, we often use orthogonal basis sets that provide near diagonal operator matrices. This often makes results conceptually simpler to understand.

# Bandstructure

To start take a simple example of a chain of  $N$  atoms:



and assume only one orbital at each atomic site for now. Use these orbitals as our basis set. Ignoring overlap, we have a diagonal Hamiltonian matrix of size  $N \times N$ :

$$H = \begin{bmatrix} E_0 & & & & \\ & E_0 & & & \\ & & \ddots & & \\ & & & \ddots & \\ & & & & E_0 \end{bmatrix} \quad (\text{ignoring overlap})$$

$N \times N$

If atoms are brought close together, overlap occurs. So we will have non-zero off-diagonal elements in  $[H]$ , like what we had in Hydrogen molecule.

$$H = \begin{bmatrix} E_0 & E_{ss} & & & \\ E_{ss} & E_0 & E_{ss} & & \\ & E_{ss} & E_0 & E_{ss} & \\ & & E_{ss} & E_0 & \ddots \\ & & & \ddots & \ddots \end{bmatrix}$$

The rows are identical due to the periodicity of the lattice.

So our basic equations to solve are:

$$E \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \\ \vdots \\ \psi_N \end{bmatrix} = \begin{bmatrix} E_0 & E_{ss} & & & \\ E_{ss} & E_0 & E_{ss} & & \\ & E_{ss} & E_0 & E_{ss} & \\ & & E_{ss} & E_0 & \ddots \\ & & & \ddots & \ddots \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \\ \vdots \\ \psi_N \end{bmatrix}$$

Periodicity at end points  
↓  
 $E_{ss}$

where:  $E\psi_n = E_{ss}\psi_{n-1} + E_0\psi_n + E_{ss}\psi_{n+1}$

This equation can be solved by assuming  $\psi_n = \psi_0 e^{in\phi}$  where  $\phi$  can be any real number.

$$\Rightarrow E = E_{ss} \frac{\psi_{n-1}}{\psi_n} + E_0 + E_{ss} \frac{\psi_{n+1}}{\psi_n}$$

substitute  $\Rightarrow E = E_{ss} e^{-i\phi} + E_0 + E_{ss} e^{i\phi}$

$$\Rightarrow E = E_0 + 2E_{ss} \cos \phi$$

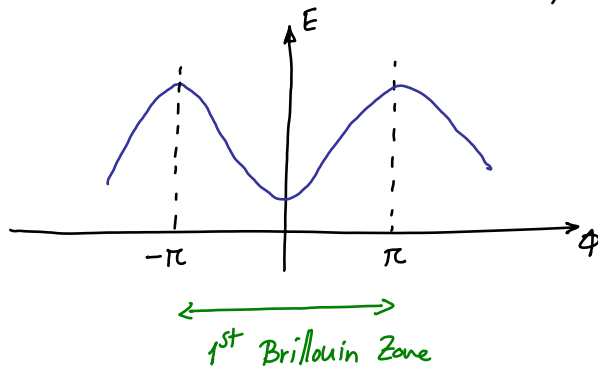
It seems we have found the energy values. However there is a problem as  $\phi$  is continuous. We must have a finite and discrete number of eigenvalues.

So we must consider (1) limit the range of  $\phi$  and (2) discretize the allowed values of  $\phi$ .

What limits the range of  $\phi$ ?

$$\psi_n = \psi_0 e^{in(\phi+2\pi)} = \psi_0 e^{in\phi}$$

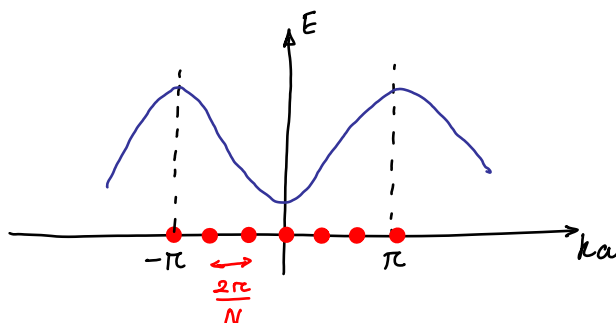
So  $\phi$  and  $\phi+2\pi$  give us the same wave function and we only need  $0 \leq \phi \leq 2\pi$



Since the lattice is periodic, we must also have:

$$\begin{aligned} \psi_{N+1} &= \psi_1 \\ \psi_0 e^{i(N+1)\phi} &= \psi_0 e^{i\phi} \Rightarrow e^{iN\phi} = 1 \Rightarrow N\phi = 2\pi m \\ \Rightarrow \phi &= m \frac{2\pi}{N} \quad m=1,2,3, \dots \end{aligned}$$

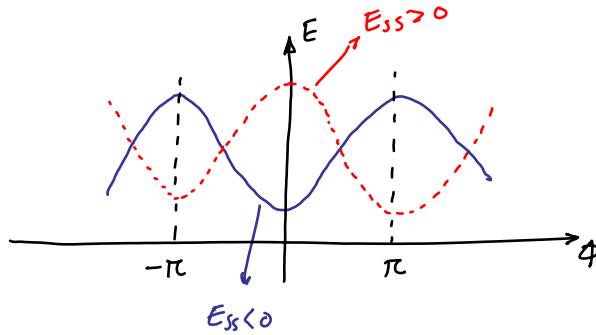
So  $\phi$  is discrete:



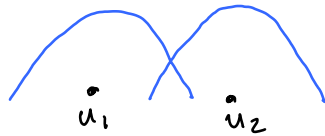
usually  $\phi$  is written as  $\phi = ka$  where 'a' is the spacing between lattice points.

How does the value of  $E_{ss}$  affect  $E$ ?

for  $E_{ss} > 0$ ,  $E$  has upward curvature in the region of  $-\pi \leq \phi \leq \pi$  and downward for  $E_{ss} < 0$ :



In general sign of  $E_{ss}$  depends on the sign of the potential and the symmetry of the overlapping orbitals. For example for 1S Hydrogen orbitals:

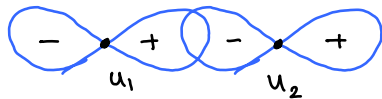


with the interaction potential  $U < 0$  (since  $U$  depends mostly on the nuclear force)

we have:

$$\int d\vec{r} \underbrace{u_1^*}_{\oplus} \underbrace{U}_{\ominus} \underbrace{u_2}_{\oplus} < 0 \rightarrow E_{ss} < 0$$

Likewise, for  $2p_x$  hydrogen orbitals we have:



$$\text{thus } \int d\vec{r} \underbrace{u_1^*}_{\oplus} \underbrace{U}_{\ominus} \underbrace{u_2}_{\oplus} > 0 \rightarrow E_{ss} > 0$$

In semiconductors the valance band is often composed of  $p'$  orbitals and the conduction band of  $s'$  orbitals. That's why we have the well known curvature:



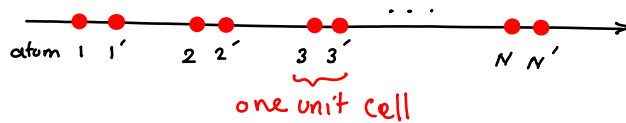
∪ CB from s-orbitals ( $E_{ss} > 0 \rightarrow +$  curvature)

∩ VB from p-orbitals ( $E_{ss} < 0 \rightarrow -$  curvature)

## Two atoms at each lattice site

What if we have 2 atoms at each lattice site:

In this case we label the atoms such as:



and the Sch. equ. becomes:

$$E \begin{bmatrix} \psi_1 \\ \psi_1' \\ \psi_2 \\ \psi_2' \\ \psi_3 \\ \psi_3' \\ \vdots \\ \psi_N \\ \psi_N' \end{bmatrix} = \begin{bmatrix} E_0 & E_{ss} & 0 & 0 & 0 \\ E_{ss} & E_0 & E_{ss}' & 0 & 0 \\ 0 & E_{ss}' & E_0 & E_{ss} & 0 & 0 \\ 0 & 0 & E_{ss} & E_0 & E_{ss}' & 0 \\ 0 & 0 & 0 & E_{ss}' & E_0 & E_{ss} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & E_{ss} & E_0 & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_1' \\ \psi_2 \\ \psi_2' \\ \psi_3 \\ \psi_3' \\ \vdots \\ \psi_N \\ \psi_N' \end{bmatrix}$$

The primary difference is  $E_{ss} \neq E_{ss}'$ , which results in only even/odd rows.

If we collect elements  $\psi_n$  and  $\psi_n'$  into the form  $\phi_n = \begin{bmatrix} \psi_n \\ \psi_n' \end{bmatrix}$  we have:

$$E \begin{bmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_N \end{bmatrix} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} & H_{23} \\ & H_{32} & H_{33} \\ \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_N \end{bmatrix}$$

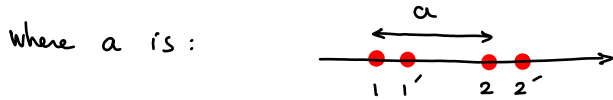
Where:

$$H_{nn} = \begin{bmatrix} E_0 & E_{ss} \\ E_{ss} & E_0 \end{bmatrix} \quad H_{n,n+1} = \begin{bmatrix} 0 & 0 \\ E_{ss}' & 0 \end{bmatrix} \quad H_{n,n-1} = \begin{bmatrix} 0 & E_{ss}' \\ 0 & 0 \end{bmatrix}$$

$$\Rightarrow E \{ \Phi_n \} = H_{n,n-1} \{ \Phi_{n-1} \} + H_{nn} \{ \Phi_n \} + H_{n,n+1} \{ \Phi_{n+1} \}$$

To solve this set of equations now apply the following trick before:

$$\{ \Phi_n \} = \{ \Phi_0 \} e^{in\phi} = \{ \Phi_0 \} e^{ikna} \quad (\text{recall } \phi = ka)$$



Substitute  $\Rightarrow$

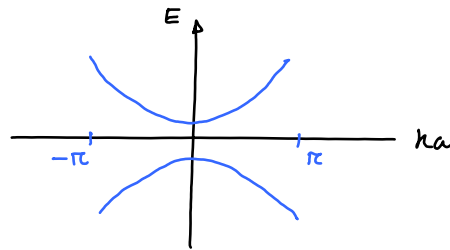
$$E \{ \Phi_0 \} e^{in\phi} = \left( [H_{n,n-1}] e^{i(n-1)ka} + [H_{n,n}] e^{in\phi} + [H_{n,n+1}] e^{i(n+1)ka} \right) \{ \Phi_0 \}$$

$\equiv [h(\vec{k})]$

Or in a simplified form:

$$E \{ \Phi_0 \} = [h(\vec{k})] \{ \Phi_0 \}$$

now the eigenvalues for each  $\vec{k}$  come in pairs:

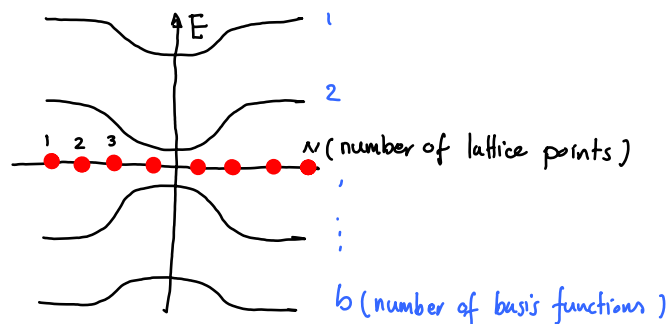


The number of eigenvalues per  $\vec{k}$  is equal to the number of basis functions (orbitals) per unit cell. Here we had two basis functions per unit cell.

Therefore, if we have 'b' basis functions, we have 'b' eigenvalues for each

$\vec{k}$ . and if we have  $N$  lattice points, this results in  $N$  different  $\vec{k}$  values,

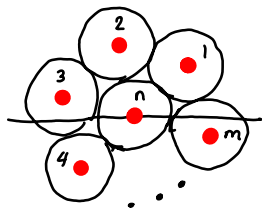
hence,  $N \cdot b$  eigenvalues overall:



## In two dimension

It is very straight forward going from 1D to higher dimensions:

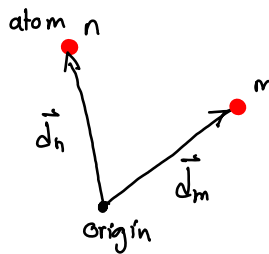
from the  $n^{\text{th}}$  unit cell we sum over all  $m$  neighboring cells:



$$\Rightarrow [h(k)] = \sum_m [H_{nm}] e^{ik(m-n)a}$$

↓  
but  $ma$  and  $na$  are positions in 1D

To generalize, pick the origin and define the positions with vectors:



Now we can write:

$$\{\Phi_n\} = \{\Phi_0\} e^{i\vec{k} \cdot \vec{d}_n}$$

which must satisfy the sch. equ. After substituting like in 1D we get:

$$E \{\Phi_0\} = [h(k)] \{\Phi_0\}$$

where  $[h(k)] = \sum_m [H_{nm}] e^{i\vec{k} \cdot (\vec{d}_m - \vec{d}_n)}$

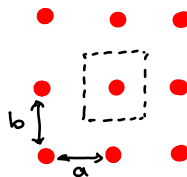
which is applicable to any number of dimensions!

All these simple results are due to the 'periodic' lattice.

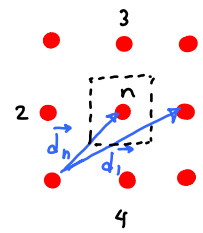
Example Rectangular lattice:

We have one basis orbital per unit cell

so  $[h(k)]$  and  $[H_{nm}]$  are  $1 \times 1$ .



Take  $\vec{k} = k_x \hat{x} + k_y \hat{y}$  and set the origin  $n$  as shown. We want  $h(\vec{k}) = \sum_m H_{nm} e^{i\vec{k} \cdot (\vec{d}_m - \vec{d}_n)}$



Evaluating  $H_{nm}$  results in  $E_0$  (self-energy) and evaluating  $H_{nm}$  results in a value that we call it 't'. So we have:

$$h(\vec{k}) = H_{nn} + H_{n1} e^{i\vec{k} \cdot (\vec{d}_1 - \vec{d}_n)} + H_{n2} e^{i\vec{k} \cdot (\vec{d}_2 - \vec{d}_n)} + H_{n3} e^{i\vec{k} \cdot (\vec{d}_3 - \vec{d}_n)} + H_{n4} e^{i\vec{k} \cdot (\vec{d}_4 - \vec{d}_n)}$$

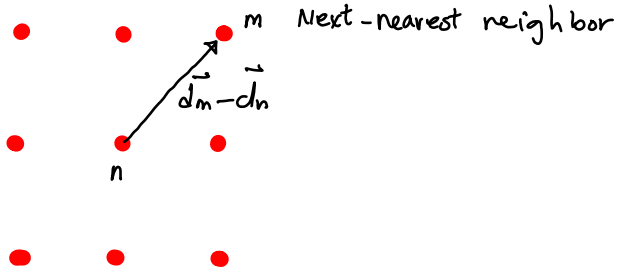
$$= E_0 + t \left( e^{ik_x a} + e^{-ik_x a} + e^{iky b} + e^{-iky b} \right)$$

$$h(\vec{k}) = E(k) = E_0 + 2t (\cos k_x a + \cos k_y b)$$

we could also go beyond nearest neighbor interactions. For example:

Now in the exponent of  $h(k)$  terms we have:

$$\vec{k} \cdot (\vec{d}_m - \vec{d}_n) = (k_x \hat{x} + k_y \hat{y}) \cdot (a\hat{x} + b\hat{y})$$

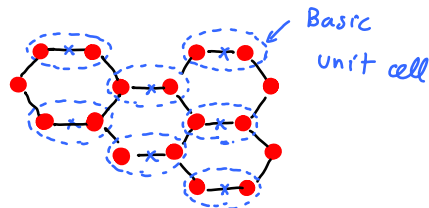


## Graphite

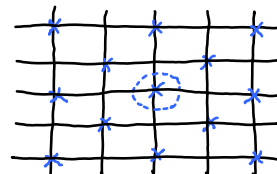
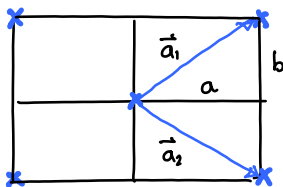
First identify the basic unit cell as shown:

define two basis vectors  $\vec{a}_1$  and  $\vec{a}_2$  such that the position of any cell in the lattice can

be written as:  $\vec{R} = m\vec{a}_1 + n\vec{a}_2$   $m, n$  are integers.



The lattice structure only repeats in pairs of 2!

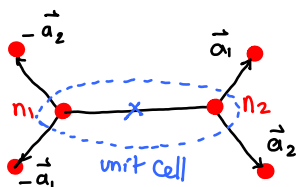


Let's assume one orbital (basis function) per carbon atom. This gives two basis functions per unit cell. So  $[h(\vec{k})]$  is  $2 \times 2$  matrix.

Let  $t$  again denote the overlap between 2 adjacent (nearest neighbor) carbon atoms. Call the atoms  $n_1$  and  $n_2$  in the unit cell. So  $H_{nn}$  is:

$$H_{nn} = \begin{matrix} n_1 \rightarrow & \begin{bmatrix} E_0 & t \\ t & E_0 \end{bmatrix} \\ n_2 \rightarrow & \end{matrix}$$

Overlap outside the unit cell will involve 4 nearest atoms:



So we must add 4 more matrices with their phase factor:

$$\begin{bmatrix} 0 & 0 \\ t & 0 \end{bmatrix} e^{i\vec{k} \cdot \vec{a}_1} + \begin{bmatrix} 0 & t \\ 0 & 0 \end{bmatrix} e^{i\vec{k} \cdot (-\vec{a}_2)} + \begin{bmatrix} 0 & t \\ 0 & 0 \end{bmatrix} e^{i\vec{k} \cdot (-\vec{a}_1)} + \begin{bmatrix} 0 & 0 \\ t & 0 \end{bmatrix} e^{i\vec{k} \cdot \vec{a}_2}$$

The final matrix looks like:

$$[h(\vec{k})] = \begin{bmatrix} E_0 & t(e^{-i\vec{k} \cdot \vec{a}_1} + e^{-i\vec{k} \cdot \vec{a}_2} + 1) \\ t(e^{i\vec{k} \cdot \vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2} + 1) & E_0 \end{bmatrix}$$

$$\text{Let: } \begin{cases} \vec{a}_1 = a\hat{x} + b\hat{y} \\ \vec{a}_2 = a\hat{x} - b\hat{y} \end{cases} \rightarrow [h(\vec{k})] = \begin{bmatrix} E_0 & h_0^* \\ h_0 & E_0 \end{bmatrix}$$

$$\text{where } h_0 = t(1 + e^{i(k_x a + k_y b)} + e^{i(k_x a - k_y b)})$$

We must now find the eigenvalues of  $[h(\vec{k})]$ . Recall for a

$2 \times 2$  matrix of the form:

$\begin{bmatrix} a & b^* \\ b & a \end{bmatrix}$  the eigenvalues are  $a \pm |b|$ .

So the eigenvalues of  $[h(\vec{k})]$  are  $E_0 \pm |h_0|$ . What is  $|h_0|$ ?

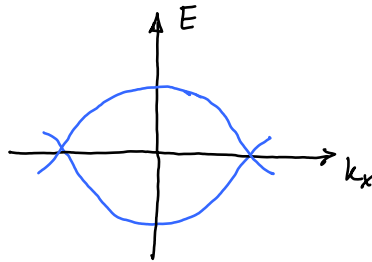
well,  $h_0 = t(1 + 2e^{ik_x a} \cos k_y b)$  as we derived.  $\Rightarrow$

$$h_0 h_0^* = t^2 (1 + 4 \cos k_x a \cos k_y b + 4 \cos^2 k_y b) = |h_0|^2$$

$$\rightarrow |h_0| = t \sqrt{1 + 4 \cos k_x a \cos k_y b + 4 \cos^2 k_y b}$$

$$E(\vec{k}) = E_0 \pm |h_0|$$

If we plot  $E(\vec{k})$ , we see the exactly symmetric two eigenvalues:



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## Graphite and Diamond

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Diamond is an example for a 3D lattice. Diamond is also made of Carbon. So why graphite and diamond have such different properties?

### Graphite

- Parallel 2D planes.  
Loose coupling between planes.
- In-plane electrical conductivity  
100 times better than perpendicular
- $sp^2$  bonding

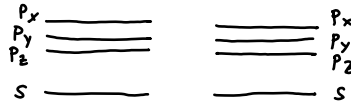
### Diamond

- Hardest material
- Poor conductor
- $sp^3$  bonding

The answer lies in the interaction of the carbon valence orbitals  $2s^2p^2$ .

Carbon valence orbitals:

2 - atoms in unit cell



In graphite the  $p_z$  orbitals are completely decoupled from

$s, p_x,$  and  $p_y$  orbitals. Hence, the Hamiltonian matrix looks like:

$$H = \begin{bmatrix} \begin{matrix} s & p_x & p_y \\ \begin{bmatrix} \phantom{s} & \phantom{p_x} & \phantom{p_y} \end{bmatrix} & & \\ & & p_z \\ & & 0 \end{matrix} \\ 0 & \begin{bmatrix} \phantom{s} & \phantom{p_x} & \phantom{p_y} \end{bmatrix} \end{bmatrix} \quad \text{Block diagonal matrix.}$$

meaning  $\int d\vec{r} u_{s,p_x,p_y} \hat{H} u_{p_z} = 0$

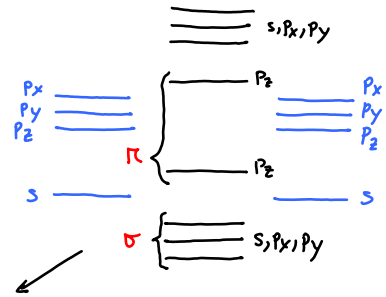
In case of diamond, the  $p_z$  orbitals are not decoupled and:

$$\int d\vec{r} u_{s,p_x,p_y} \hat{H} u_{p_z} \neq 0$$

So the bonding levels of graphite are:

$s, p_x, p_y$  bonds are called  $\sigma$ -bonds and the

$p_z$  bonds are called  $\pi$ -bonds.



Why are the  $s, p_x, p_y$  bonds lower than  $p_z$  bond?

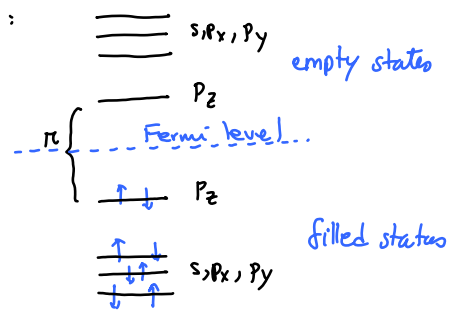
This is because the  $s, p_x, p_y$  levels overlap more:

$$\left| \int d\vec{r} u_{s,p_x,p_y} \hat{H} u_{s,p_x,p_y} \right| > \left| \int d\vec{r} u_{p_z} \hat{H} u_{p_z} \right|$$

Giving rise to bigger overlap matrix elements  $M$ :

$$\begin{bmatrix} \epsilon & M \\ M & \epsilon \end{bmatrix} \Rightarrow 2M \begin{matrix} \text{---} \epsilon + M \\ \text{---} \epsilon - M \end{matrix}$$

Fermi level lies between the  $\pi$  levels in Graphite:



Since conduction depends on the states right around Fermi energy, the optical and electrical properties of graphite are largely determined by the  $p_z$   $\pi$  levels:

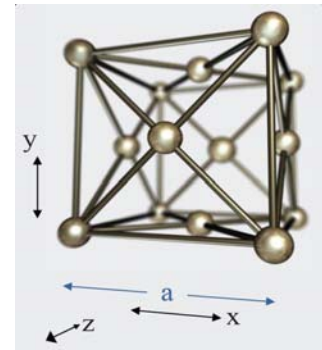
So it is the mixing of orbitals during bonding which results such different properties for diamond and graphite.

## Semiconductors Bandstructures

Common semiconductors have an FCC structures.

In common semiconductors, like GaAs, we have two overlapping (interlocked) FCC lattices

(since there are two atoms, like Ga & As, per unit cell).



For example to get the one for GaAs, 1) Take an FCC

lattice 2) Duplicate it 3) Finally move the duplicate one by  $\frac{1}{4}$  the length of body diagonal along the body diagonal.

The unit vectors of an FCC lattice can be defined as:

$$\vec{a}_1 = (\hat{x} + \hat{y}) \frac{a}{2}$$

$$\vec{a}_2 = (\hat{y} + \hat{z}) \frac{a}{2}$$

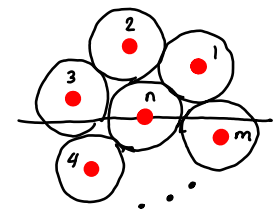
$$\vec{a}_3 = (\hat{x} + \hat{z}) \frac{a}{2}$$

So the position of any unit cell is:

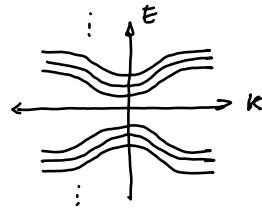
$$\vec{R} = m\vec{a}_1 + n\vec{a}_2 + p\vec{a}_3 \quad m, n, p \text{ are integers.}$$



To calculate  $[h(k)]$ , again consider the unit cell  $n$ , and its  $m$  nearest neighbors.

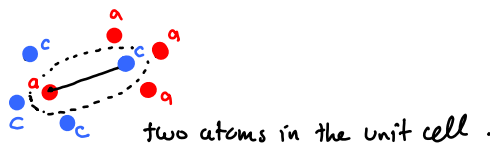


From  $[h(k)]$  we get the eigenenergies of our periodic lattice. These eigen-energies form the levels commonly known as band structure.



In general we must consider multiple orbitals in 3D. Let's start simple and only consider s orbitals.

We have two atoms in the unit cell an 'cation' (c) and 'anion' (a):



Such that an anion has only 4 cations as nearest neighbors and same for a cation.

So the first s-orbital matrix is:

$$\begin{matrix} S_c & S_a \\ S_c & \begin{bmatrix} E_{sc} & E_{ss} \\ E_{ss} & E_{sa} \end{bmatrix} \end{matrix} \quad \text{for } m=n$$

The first cation to anion s overlap matrix is:

$$\begin{matrix} S_c & S_a \\ S_c & \begin{bmatrix} 0 & E_{sa} \\ 0 & 0 \end{bmatrix} \end{matrix} e^{i\vec{k} \cdot \vec{a}_1} \quad m \neq n$$

Adding all other cation to anion matrices we get:

$$\begin{matrix} S_c & S_a \\ S_c & \begin{bmatrix} 0 & E_{sa} \\ 0 & 0 \end{bmatrix} \end{matrix} (e^{i\vec{k} \cdot \vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2} + e^{i\vec{k} \cdot \vec{a}_3})$$

Similarly all anion to cation s overlap matrices give:

$$\begin{pmatrix} 0 & 0 \\ E_{ss} & 0 \end{pmatrix} \begin{pmatrix} -i\vec{k}\cdot\vec{a}_1 & -i\vec{k}\cdot\vec{a}_2 & -i\vec{k}\cdot\vec{a}_3 \\ e & +e & +e \end{pmatrix}$$

The total s overlap matrix is:  $\begin{bmatrix} E_{sc} & E_{ss}g_0 \\ E_{ss}g_0^* & E_{sa} \end{bmatrix}$  where:  $g_0 = 1 + e^{i\vec{k}\cdot\vec{a}_1} + e^{i\vec{k}\cdot\vec{a}_2} + e^{i\vec{k}\cdot\vec{a}_3}$

Altogether the full matrix looks like:

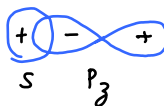
$$\begin{matrix} & S_c & S_a & P_x^c & P_y^c & P_z^c & P_x^a & P_y^a & P_z^a \\ \begin{matrix} S_c \\ S_a \\ P_x^c \\ P_y^c \\ P_z^c \\ P_x^a \\ P_y^a \\ P_z^a \end{matrix} & \left[ \begin{array}{cccccccc} E_{sc} & E_{ss}g_0 & 0 & 0 & 0 & E_{scpa}g_1 & E_{scpa}g_2 & E_{scpa}g_3 \\ E_{ss}g_0^* & E_{sa} & E_{sapc}g_1^* & E_{sapc}g_2^* & E_{sapc}g_3^* & 0 & 0 & 0 \\ 0 & E_{sapc}g_1 & E_{pc} & 0 & 0 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\ 0 & E_{sapc}g_2 & 0 & E_{pc} & 0 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\ 0 & E_{sapc}g_3 & 0 & 0 & E_{pc} & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \\ E_{scpa}g_1^* & 0 & E_{xx}g_0^* & E_{xy}g_3^* & E_{xy}g_2^* & E_{pa} & 0 & 0 \\ E_{scpa}g_2^* & 0 & E_{xy}g_3^* & E_{xx}g_0^* & E_{xy}g_1^* & 0 & E_{pa} & 0 \\ E_{scpa}g_3^* & 0 & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_0 & 0 & 0 & E_{pa} \end{array} \right] \end{matrix}$$

Note that  $g_1, g_2, g_3$  terms differ only from the  $g_0$  term by a  $\oplus$

or  $\ominus$  sign. For example:

$$g_1 = 1 + e^{i\vec{k}\cdot\vec{a}_1} - e^{i\vec{k}\cdot\vec{a}_2} - e^{i\vec{k}\cdot\vec{a}_3}$$

$$g_2 = 1 - e^{i\vec{k}\cdot\vec{a}_1} + e^{i\vec{k}\cdot\vec{a}_2} - e^{i\vec{k}\cdot\vec{a}_3}$$

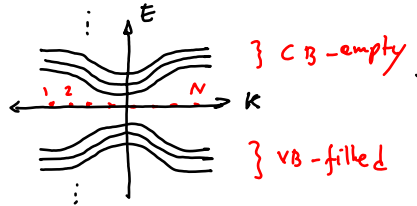
$$g_3 = 1 - e^{i\vec{k}\cdot\vec{a}_1} - e^{i\vec{k}\cdot\vec{a}_2} + e^{i\vec{k}\cdot\vec{a}_3}$$


The  $s, p_x, p_y, p_z$  orbitals give the minimum basis set needed to describe semiconductor behavior. However, often 4 orbitals are not sufficient to describe conduction. So in practice a 5th "s" orbital is also incorporated, this is known as  $sp^3s^*$  model and produces a  $10 \times 10$  rather than  $8 \times 8$  matrix  $[h(\vec{k})]$  (Refer to equ. 5.3.3 page 118 of the book).

How do the electrons are filled in the bands?

If, for example, we are modeling a lattice with 4 basis per atom (8 per unit cell)

and  $N$  unit cells then our  $k$  axis will have  $N$  points with 8 eigen-energies per point.



For silicon, with 4 basis orbitals per atom and a total of 8 per unit cell, there will be a total of  $8N$  electrons. Including spin degeneracy  $8N$  electrons occupy  $4N$  states or the 1<sup>st</sup> 4 levels in the band diagram.