IV. Electronic Energy Bands: Basic Ideas

- Related to Bonding (how atoms come together to form molecules/solids)
- Different (chemistry and physics) pictures (same results)
- Periodicity: $\{\vec{R}'s\} \leftrightarrow \underbrace{\{\vec{G}'s\}}_{\text{reciprocal space, B.Z.'s, ...}}$

⇒ look at "energy dispersion relations" $E(\vec{k})$

E ← allowed values of energy for electrons in solid

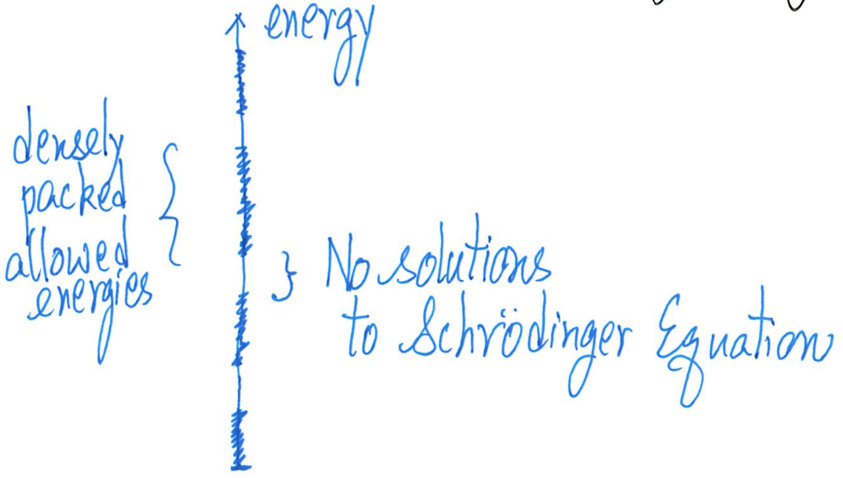
$\vec{k}$ ← wavevector living in 1/length (reciprocal) space

This is the Band Structure OR Electronic Structure Problem

- No periodicity: Molecules, $\underbrace{\text{Amorphous}}_{\text{非晶態}}$ semiconductors, alloys $Ga_xAl_{1-x}As$

⇒ still "legal" to look at how allowed energies distribute along energy axis

So, allowed energies grouped into bands separated with gaps



Not only a property of periodic systems
(Key Message #1)

Key Message #2

- Need Quantum Mechanics to understand molecules and solids

after all, a big big molecule!

A. The Single-Electron Problem of a Crystalline Solid

- Reduce problem to single-electron problem

TISE of a solid problem is: electron sees a periodic potential energy function

$$\left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + \underbrace{U(\vec{r})}\right]\psi(\vec{r}) = E\,\psi(\vec{r}) \qquad (1)$$

$U(\vec{r}+\vec{R}) = U(\vec{r})$ defines periodic[+] potential energy function

$\vec{R}$: lattice vectors

Solutions give the allowed energies to an electron under the influence of a periodic potential energy function

then fill electrons into these states according to fermionic requirement

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[+] The Periodicity is governed by the Lattice Vectors of the Bravais Lattice of the crystal

This is the $\underbrace{\text{Electronic Energy Band problem!}}$

To solve for $E \leftrightarrow \psi(\vec{r})$ Pairs!

labelled by

bands separated by gaps $\leftarrow \, < E_n(\vec{k})$

in reciprocal space

labelled by $\underbrace{\psi_{n\vec{k}}(\vec{r})}_{\text{Bloch States}}$

- Many features of the solutions are common to periodic $U(\vec{r})$'s
- Great success! [Explained why there are conductors, insulators, semiconductors]

So Success to the extent that...

Why does it work become a question!

B. The Big and Impossible Problem of the Solid State

$N \sim 10^{23}$ ions [Momenta and Coordinates]

$n \sim 10^{24}$ electrons [Momenta and Coordinates]

electron-electron, electron-ion, ion-ion interactions

$$\hat{H} = \Big[\underbrace{\sum_{k=1}^{N} -\frac{\hbar^2}{2M_k}\nabla^2_{\vec{R}_k}}_{\substack{\text{k.e. of ions} \\ \text{(N of them)}}} \underbrace{-\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\vec{r}_i}}_{\substack{\text{k.e. of electrons} \\ \text{(n of them)}}} + \underbrace{\frac{1}{2}{\sum_{i,j=1}^{n}}' \frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{\substack{\text{el-el interaction} \\ \text{(p.e.) [repulsive]}}} + \underbrace{V_{ii}(\vec{R}_1,\cdots;\vec{R}_N)}_{\substack{\text{ion-ion interaction} \\ \text{(p.e.) repulsive}}} + \underbrace{V_{ei}(\vec{r}_1,\cdots\vec{r}_n;\vec{R}_1,\cdots;\vec{R}_N)}_{\substack{\text{electron-ion} \\ \text{(p.e.) (attractive)}}} \Big]$$

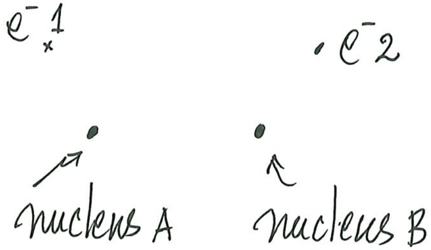
$$\hat{H}\,\underset{\text{(big molecule)}}{\Psi_{solid}}(\vec{r}_1,\cdots\vec{r}_n;\vec{R}_1,\cdots,\vec{R}_N) = E\,\underset{\text{(big molecule)}}{\Psi_{solid}}\underbrace{(\vec{r}_1,\cdots;\vec{r}_n;\vec{R}_1,\cdots;\vec{R}_N)}_{\sim 10^{25}\text{ variables!}} \qquad (2)$$

$+{\sum_{i,j=1}^{n}}'(\,)$ means $i \neq j$

Impossible to Solve! But this is THE real solid QM problem.

C. Diatomic Molecular Problems: Copying ideas

- Don't feel bad! Even the four-particle problem of H_2 molecule cannot be solved



$$\Bigg[-\frac{\hbar^2}{M}\nabla^2_{\vec{R}_A}-\frac{\hbar^2}{M}\nabla^2_{\vec{R}_B}-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_1}-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2}+\overbrace{\frac{e^2}{4\pi\varepsilon_0|\vec{R}_A-\vec{R}_B|}}^{V_{ii}}$$

$$+\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{R}_A|}-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{R}_B|}$$

$$-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{R}_A|}-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{R}_B|}\Bigg]\Psi_{molecule}(\vec{r}_1,\vec{r}_2;\vec{R}_A,\vec{R}_B)$$

$$=E_{molecule}\,\Psi_{molecule}(\vec{r}_1,\vec{r}_2;\vec{R}_A,\vec{R}_B) \qquad (3)$$

Equation for allowed energies $E_{molecule}$ of the whole molecule.

The TISE is completely analogous to the solid problem (but only with 4 particles)

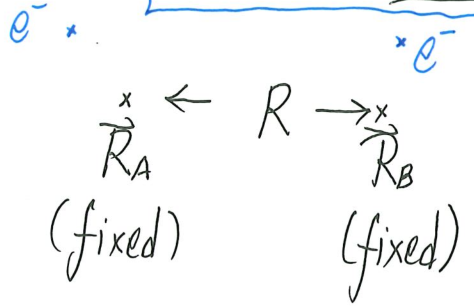
Ways Forward

- Decouple the electronic and the ionic quantum mechanical problems
  ↑ an approximation (Born-Oppenheimer approximation)

$$\Psi_{\text{molecule}} \cong \psi_{\text{electronic}}(\vec{r}_1, \vec{r}_2; \underbrace{\vec{R}_A, \vec{R}_B}_{\text{as parameters [not dynamical variables]}}) \cdot \varphi_{\text{ions}}(\overbrace{\vec{R}_A, \vec{R}_B}^{\text{as dynamical variables}}) \qquad (4)$$

- Practically, the approximation means that in considering the electronic Schrödinger problem (related to electrons)

$\boxed{\text{assume ions to be fixed}}$



$$\hat{H}_{\text{electronic}} = \Big[\frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2} \overbrace{- \frac{e^2}{4\pi\varepsilon_0}\Big[\frac{1}{|\vec{r}_1 - \underset{\text{fixed}}{\vec{R}_A}|} + \frac{1}{|\vec{r}_1 - \underset{\text{fixed}}{\vec{R}_B}|} + \frac{1}{|\vec{r}_2 - \underset{\text{fixed}}{\vec{R}_A}|} + \frac{1}{|\vec{r}_2 - \underset{\text{fixed}}{\vec{R}_B}|}\Big]}^{\text{This is the } V_{ei} \text{ part}} + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \Big] \qquad (5)$$

$$\hat{H}_{\text{electronic}}\, \psi_{\text{electronic}}(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B) = E_{\text{electronic}}\, \psi_{\text{electronic}}(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B) \qquad (6)$$

- Even so, Eq.(6) is still hard to solve due to the $+\dfrac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ electron-electron interaction term

- Reduce to single-electron problem by
  - regarding one electron being influenced by the other electron in an averaged ("mean field" OR "effective field") way (under the names of Hartree and Hartree-Fock approximations)

- Even so, the V_{ei} part requires further work[+] when more complicated (bigger) atoms are involved

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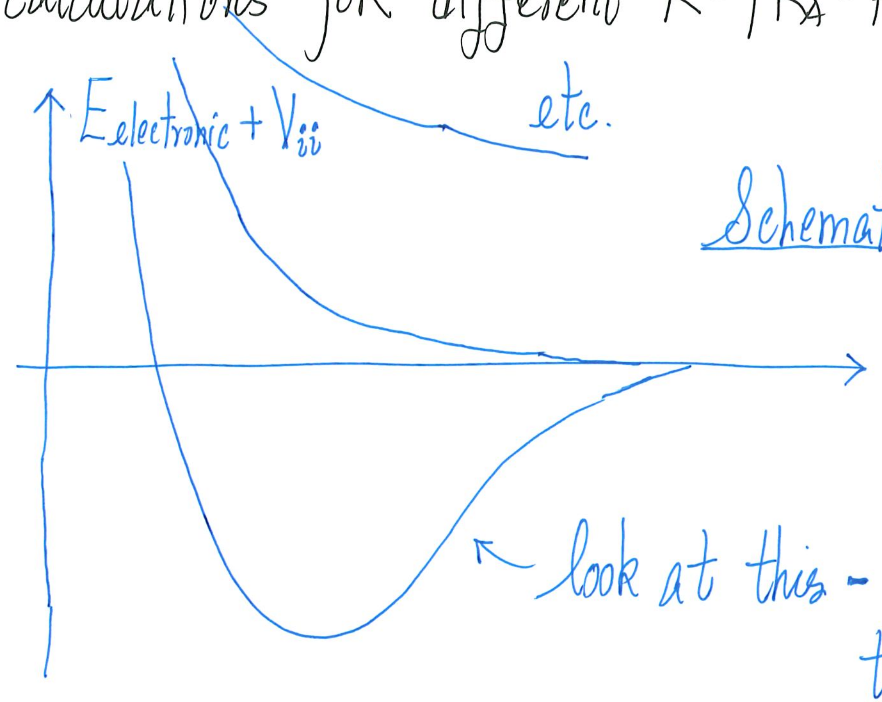
[+] Density functional Theory (DFT) helps in this aspect. A related idea is pseudopotentials.

- Given R, one electronic problem (this will become the Energy Band Problem)
- Repeat calculations for different $R = |\vec{R}_A - \vec{R}_B|$ ⇒ Many $E_{\text{electronic}}$ values for each R

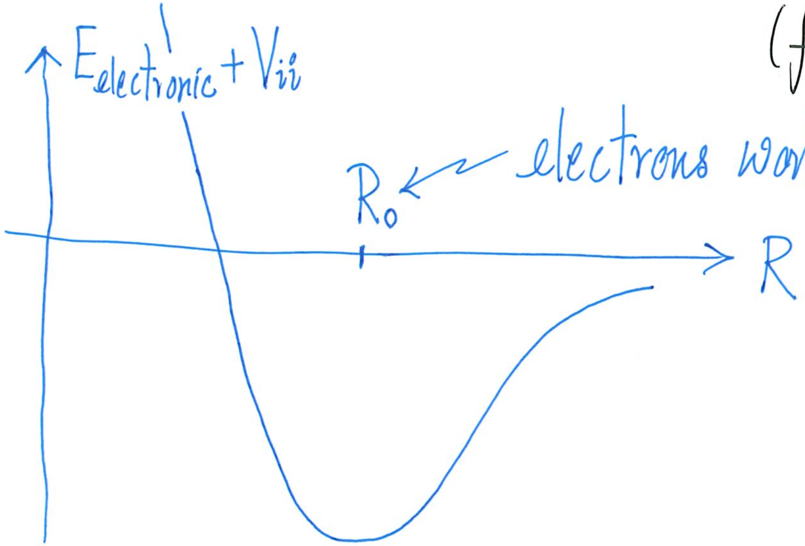


<u>Schematic</u>

$$V_{ii} = \frac{e^2}{4\pi\varepsilon_0 R}$$

look at this – there are only 2 electrons, so this curve matters

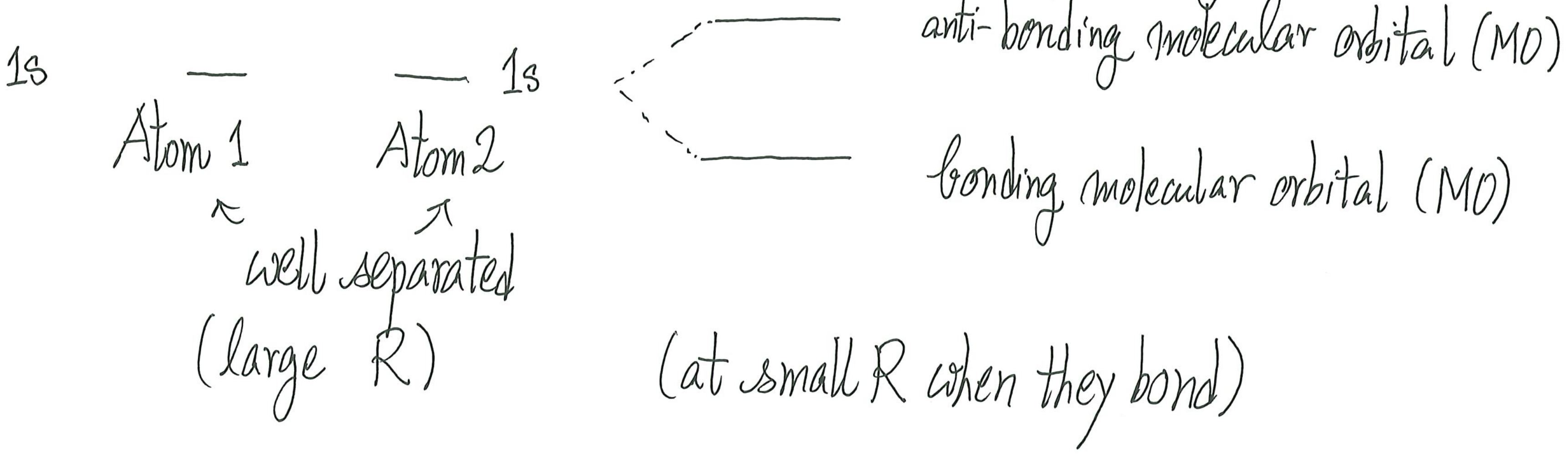
(fill in according to <u>Pauli Exclusion rule</u>)



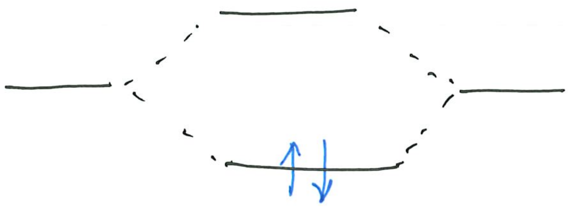
electrons work to suggest an equilibrium separation (this is <u>Bonding</u>)

↑ due to electrons

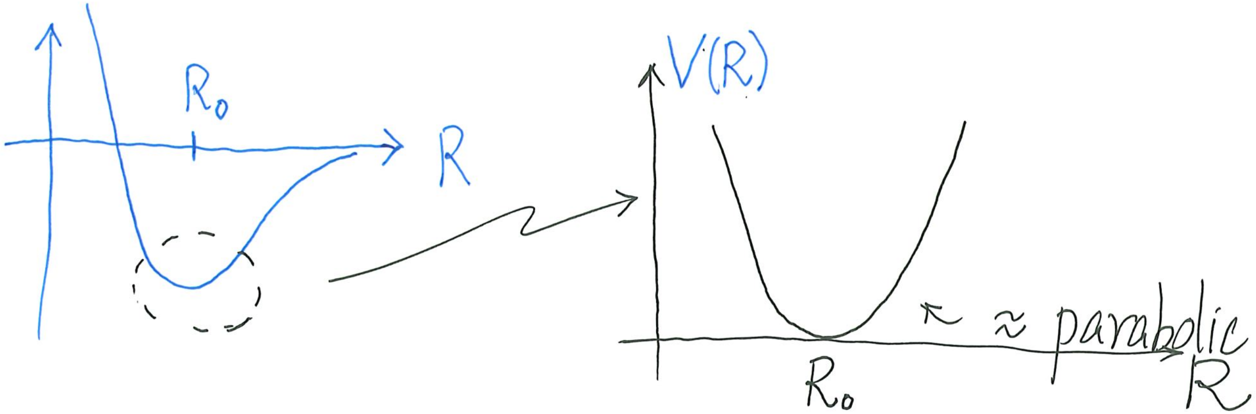
It is from here that we have the following picture ...



For H_2, filling two electrons ($m_s = +1/2, -1/2$) into bonding MO, energy is lower than two isolated (far apart) neutral atoms. This picture is often displayed as



in chemistry books about bonding. It is entirely quantum mechanical!

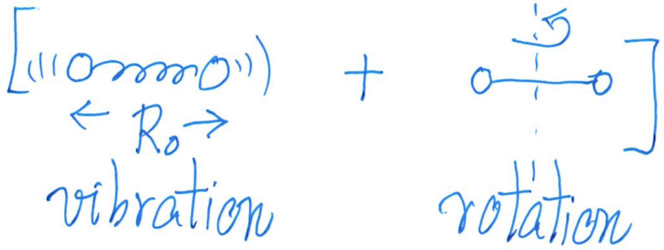


For the two nuclei, go back to consider their QM problem

let them move again

$$\left[-\frac{\hbar^2}{2M}\nabla^2_{\vec{R}_A}-\frac{\hbar^2}{2M}\nabla^2_{\vec{R}_B}+\underbrace{V(|\vec{R}_A-\vec{R}_B|)}_{\text{nuclei problem is a 3D harmonic oscillator problem}}\right]\varphi(\vec{R}_A,\vec{R}_B)=E\,\varphi(\vec{R}_A,\vec{R}_B)$$

observable in molecular spectrum →



This will become the Lattice Vibrations (phonons) problem in solids.

And we can understand much of H_2 physics (other molecules as well)

D. Let ions be fixed and focus on the electrons

(no more K.E. terms for ions)

$$\Big[\underbrace{\sum_{i=1}^{n}\frac{-\hbar^2}{2m}\nabla^2_{\vec r_i}}_{\text{k.e. of electrons}} + \underbrace{\frac{1}{2}\sum_{i,j=1}^{n}{}'\,\frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{\text{el-el}} + \underbrace{V_{el\text{-}ion}(\vec r_1,\cdots;\vec r_n;\overset{\substack{\text{fixed (as parameters)}\\ \downarrow}}{\{\vec R\}})}_{\text{el-ion}}\Big]\psi(\vec r_1,\cdots;\vec r_n;\{\vec R\})$$

$$= \underbrace{E(\{\vec R\})}_{\substack{\text{electronic energies for ions}\\ \text{sitting at } \{\vec R_1,\cdots,\vec R_N\} \text{ fixed}}}\psi(\vec r_1,\cdots,\vec r_n) \qquad (7)^+$$

- If you want to deal with this problem, you should go to

$$\underbrace{\underline{\text{Many-Body Theory}}}_{\text{Handling el-el interaction}}\ \ \text{OR Solid State Theory}$$

(Many-electron problem)

It is still impossible to solve!

[+] Eq.(7) is analogous to Eq.(6), but now for a solid.

- Let ions sit at their crystalline equilibrium locations

2D square lattice
[Basis of 1 atom]

ions sit at $\vec{R}_i$ ← lattice vectors

Key consequence

$V_{\text{el-ion}}$ as seen by one electron becomes Periodic

- Averaged Effects of $(n-1)$ electrons on one electron? (this is $V_{\text{el-el}}$ term)

Periodic structure → electron density in solid should be periodic

electrons' Coulomb effect felt by one electron is on average also periodic

(justified by, e.g., Hartree and Hartree-Fock approaches)

Rough picture on accounting for el-el interaction

$\underbrace{(n-1)\text{ electrons}}$ affecting one electron

↳ they filled into single-electron states $\overbrace{\psi_i(\vec{r})}^{\text{not known!}}$

$$n(\vec{r}') = \sum_{i \leftarrow (n-1)\text{ of them}} |\psi_i(\vec{r}')|^2 \qquad [\psi_i(\vec{r}) \text{ from TISE}]$$

electron # density ↗

and generates $$\underset{(\text{direct})}{U_{ee}(\vec{r})} = \underbrace{\frac{e^2}{4\pi\varepsilon_0}\int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d^3r'}_{\text{an operator } U_{ee}(\vec{r}) \text{ into TISE}}$$

[Note that $U_{ee}(\vec{r})$ needs $n(\vec{r})$, which needs $\psi_i(\vec{r})$ for the $(n-1)$ electrons, but solving $\psi_i(\vec{r})$ needs $U_{ee}(\vec{r})$, ... (a loop)]

[This is the Hartree approach (Direct Coulomb)]

(A self-consistent approach)

Even so, the form of $V_{ei}(\vec{r})$ inside $U(\vec{r})$ is a problem.

Formally, if we consider every electron in the k.e. term, then

$$V_{ei}(\vec{r}) = \sum_{\substack{\text{all } \vec{R}\text{'s} \\ (\vec{R}_n)}} V_{nuclei}(\vec{r}-\vec{R}_n) = -\sum_{\text{all } \vec{R}_n} \frac{Ze^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_n|}$$

↑ due to array of nuclei

↑ its p.e. term's contribution at $\vec{r}$

↑ nucleus at $\vec{R}_n$

(looks straight-forward!)

But is it clever?

- Will the tightly bounded atomic states (e.g. 1s of sodium) matter for the bonding and properties of a solid?
- $r \rightarrow \vec{R}_n$, $V_{ei}(\vec{r}) \rightarrow -\infty$! Hard to deal with computationally!

  ↑ every location where nuclei sit

∴ Form of $V_{ei}(\vec{r})$ has been a big subject over decades!

Only after all these simplifications (approximations), we arrive at the single-electron problem of electronic energy bands given by

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + U(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r}) \qquad (1)$$

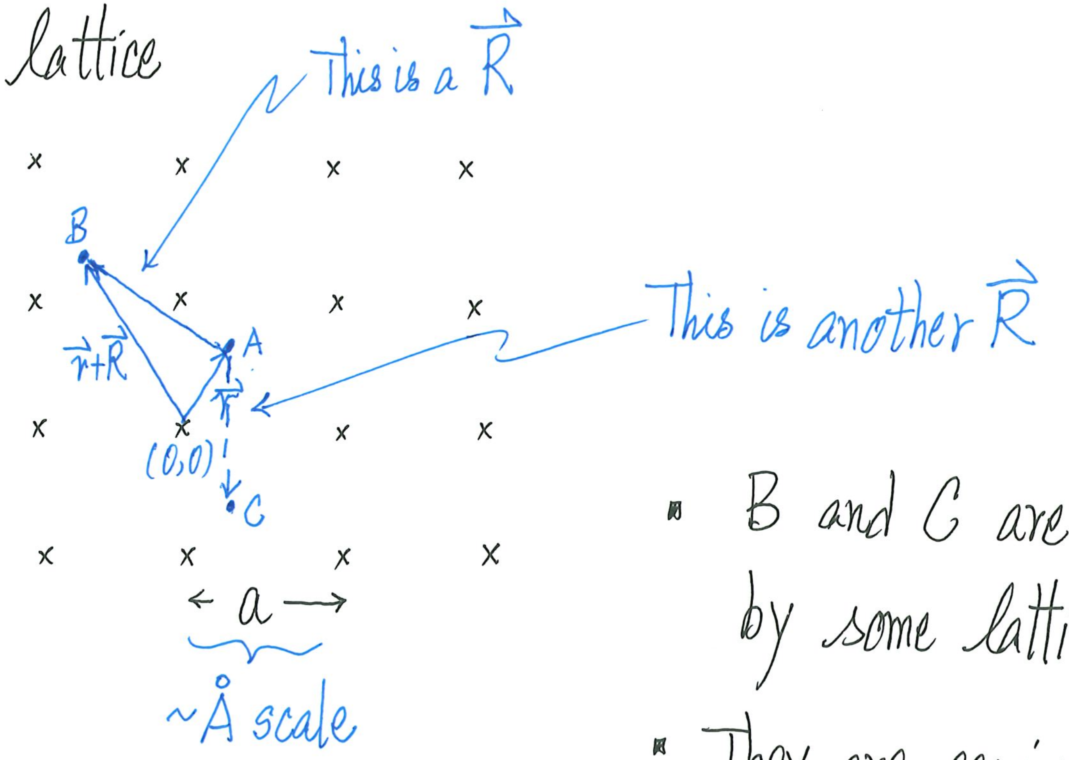
where

$$U(\vec{r}+\vec{R}) = U(\vec{r}) \qquad (8)$$

This is asking for the allowed electron states under the influence of a periodic $U(\vec{r})$ [direct lattice's $\{\vec{R}\}$ comes in] and the corresponding allowed values of energy.

The band problem (Eq.(1)+Eq.(8)) defined this way emphasizes periodicity.

2D square lattice



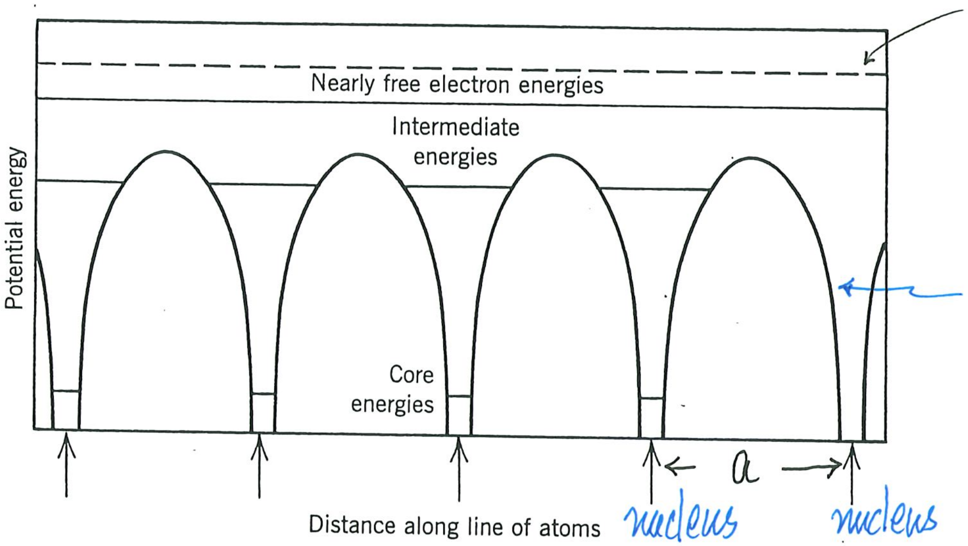
- B and C are related to A by some lattice vector $\vec{R}$
- They are $\underbrace{\text{equivalent points}}_{\text{having the same environment}}$ in a solid (infinite solid)

An electron feels the same U at points A, B, C

$$(\therefore U(\vec{r}) = U(\vec{r}+\vec{R}))$$

We need a 4D plot for $U(\vec{r})$. To get a sense, consider how $U(\vec{r})$ looks like schematically along a line of atoms in a crystal.

- For electrons here, nearly free electron behavior modulated by $U(\vec{r})$ →
- Overlapping of atomic wavefunctions ⇒ wider bands →
- Core electrons in atom have energies deep in the potential well (thus atomic wavefunctions don't overlap much)



energy just outside the solid (vacuum level)

periodic $U(r)$

Electron potential energy along a line of atoms in a crystal. The dotted line indicates the energy for an electron outside the solid. Positions of nuclei are marked by arrows and representative allowed energy levels are shown as solid horizontal lines. Core states have energies deep in the potential wells near each nucleus. Nearly free electrons have energies well above the potential energy maxima.

$a \sim$ few Å

This leads to different viewpoints (approaches) in handling the energy band problem (Eq.(1) + Eq.(8))

Take-Home Messages

- Know what the energy band problem (Eq. (1) + Eq. (8)) is about
- Appreciate the simplifications made to the real actual problem (c.f. Eq. (2))
  - Born-Oppenheimer approximation (let ions/nuclei be fixed)
  - Turn into One-electron problem (one-electron approximation)
  - Periodicity
  - Only after all these, let ions/nuclei move again and treat the lattice vibrations

The next time you see Eq. (1) + Eq. (8), appreciate that
"it is <u>NOT</u> that simple"

Then, you will appreciate better all the results and the fact that <u>the approach works</u>!

C. The Bloch's Theorem

Solutions to Single-electron Problem in Periodic $U(\vec{r})$ are of the form

$$\psi_{\vec{k}}(\vec{r}+\vec{R}_n) = e^{i\vec{k}\cdot\vec{R}_n}\,\psi_{\vec{k}}(\vec{r}) \qquad (9)$$

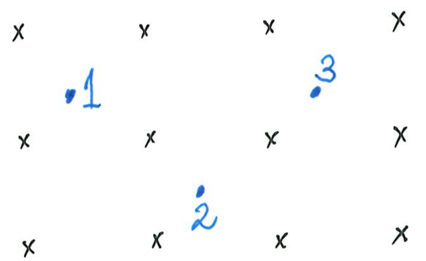
$\vec{k}$: a label of the electronic state (it lives in reciprocal space, can be restricted to be in 1st B.Z.)

$\vec{R}_n$: any lattice vector $\vec{R}_n$

(This is one form of the Bloch's Theorem[+])

[+] Felix Bloch was the first PhD student of Heisenberg (so Bloch did much on magnetism). His thesis was about the Quantum Theory of solids (using Schrödinger's wave mechanics!). His theorem was published in 1928. He won the Nobel Prize in Physics in 1952 for his work on NMR with Purcell.

(a) <u>It makes sense</u>



No reason to have different probabilities of finding electron at $\underbrace{\text{equivalent points}}_{\text{e.g. Points 1, 2, 3 (same environment)}}$ in cryal

$$|\psi(\vec{r}_1)|^2 = |\psi(\vec{r}_2)|^2 = |\psi(\vec{r}_3)|^2$$

OR $$|\psi(\underset{\uparrow}{\vec{r}})|^2 = |\psi(\vec{r}+\underset{\uparrow}{\vec{R}_n})|^2 \quad (10) \quad \text{(physics requirement)}$$

a position (somewhere) in a primitive cell

a position translated by $\vec{R}_n$ and so an equivalent point but in the primitive cell relative to the lattice point at $\vec{R}_n$

- Bloch's theorem is in line with this requirement.
- Requirement does <u>NOT</u> imply $\psi(\vec{r}) \underset{\uparrow \text{ wrong!}}{=} \psi(\vec{r}+\vec{R}_n)$

(b) It also makes sense in the trivial $U(\vec{r})$ = constant "periodic" case

$U(\vec{r})$ = constant ↗ $\left[-\frac{\hbar^2}{2m}\nabla^2 + U\right]\psi = E\psi$ free particle case

↘ can be thought to be a trivial periodic case

Solutions are plane waves:

$$\psi(\vec{r}) \sim e^{i\vec{k}\cdot\vec{r}}$$

Translate it by ANY $\vec{R}$ that lives in direct space

$$\psi(\vec{r}+\vec{R}) \sim e^{i\vec{k}\cdot\vec{R}} \cdot e^{i\vec{k}\cdot\vec{r}} \sim e^{i\vec{k}\cdot\vec{R}}\,\psi(\vec{r})$$

so it is in line with Bloch's theorem, but here for ANY $\vec{R}$

Bloch's Theorem takes this to real Periodic $U(\vec{r})$, and tells us that the translations must be those of Lattice Vectors $\vec{R}_n$.

[This is arbitrary translational (U = constant) symmetry Vs Discrete Translational symmetry]
(solids)

(c) It makes sense with all Periodic $U(\vec{r})$

Recall: A periodic function $U(\vec{r}) = \underset{\vec{G}}{\sum} U_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}$

$\vec{G}$ ← only reciprocal lattice vectors contribute

Physical meaning

Key Physical Sense

$U(\vec{r})$ only has the "power" to mix a plane wave $e^{i\vec{k}\cdot\vec{r}}$ with $e^{i(\vec{k}+\vec{G}_1)\cdot\vec{r}}$, $e^{i(\vec{k}+\vec{G}_2)\cdot\vec{r}}$, ... (generally) $e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$, ...

When we construct a solution to the band problem using superposition of plane waves, we have

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} \underbrace{C_{\vec{G}}}_{\substack{\uparrow \\ \text{the coefficients (found by solving the Schrödinger Equation (Eq.(1))}}} \underset{\nwarrow \text{ a reminder that a } \vec{k} \text{ is chosen}}{(\vec{k})}\; e^{\overbrace{i(\vec{k}+\vec{G})\cdot\vec{r}}^{\text{once a } \vec{k} \text{ is chosen, only these plane waves contribute}}} \qquad (11)$$

[This is another form of writing Bloch functions]

Write as $\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}+\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$ (12) (∵ periodicity)

Translate it by any lattice vector $\vec{R}_n$:

$$\psi_{\vec{k}}(\vec{r}+\vec{R}_n) = \sum_{\vec{G}} C_{\vec{k}+\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot(\vec{r}+\vec{R}_n)}$$

$$= \sum_{\vec{G}} C_{\vec{k}+\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}}\, \underbrace{e^{i\vec{k}\cdot\vec{R}_n}}_{\text{not involved in the sum (take it outside)}}\, \overbrace{e^{i\vec{G}\cdot\vec{R}_n}}^{\text{equals 1 for all } \vec{G}\text{'s in the sum}}$$

$$= e^{i\vec{k}\cdot\vec{R}_n}\left(\sum_{\vec{G}} C_{\vec{k}+\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}}\right)$$

$$= e^{i\vec{k}\cdot\vec{R}_n}\, \psi_{\vec{k}}(\vec{r})$$

this is the Bloch's Theorem

This is a proof of the Bloch's Theorem, as the expansion of $\psi_{\vec{k}}(\vec{r})$ is general for periodic $U(\vec{r})$.

(d) An Equivalent Form of the Bloch's Theorem

Bloch's Theorem also means that the Solutions to the energy band problem are of the form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r}) \qquad (12)$$

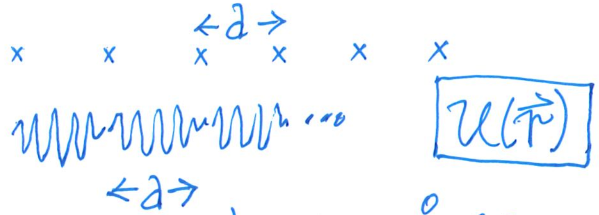
with $u_{\vec{k}}(\vec{r})$ being a periodic function of the same period as the crystal structure (lattice), i.e.

$$u_{\vec{k}}(\vec{r}+\vec{R}_n) = u_{\vec{k}}(\vec{r}) \qquad (13)$$

- This is up to a normalization constant
- This is called the "Bloch form"
- $u_{\vec{k}}(\vec{r})$: "cell function" OR "periodic part of the Bloch function"

Check:
$$\psi_{\vec k}(\vec r+\vec R_n) = e^{i\vec k\cdot(\vec r+\vec R_n)}\underbrace{u_{\vec k}(\vec r+\vec R_n)}_{=\,u_{\vec k}(\vec r)\ \text{(periodic)}}$$
$$= e^{i\vec k\cdot\vec R_n}\, e^{i\vec k\cdot\vec r}\, u_{\vec k}(\vec r)$$
$$= e^{i\vec k\cdot\vec R_n}\,\psi_{\vec k}(\vec r)$$
as required by the other form

Bloch Form
$$\psi_{\vec k}(\vec r) = \underbrace{e^{i\vec k\cdot\vec r}}_{\substack{\text{plane wave}\\ \text{(as in free particle)}}}\ \underbrace{u_{\vec k}(\vec r)}\ \rightarrow$$

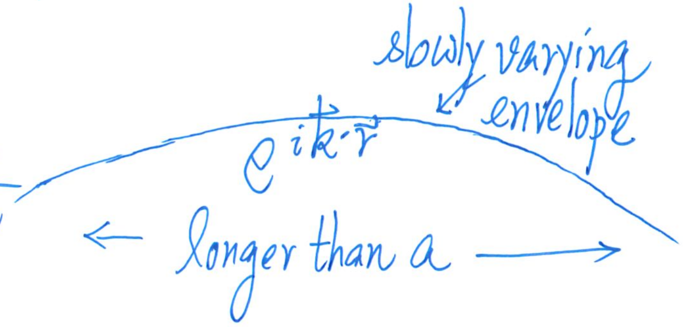


periodic on ~Å (a) scale

e.g. $\vec k$ close to 1st B.Z. center

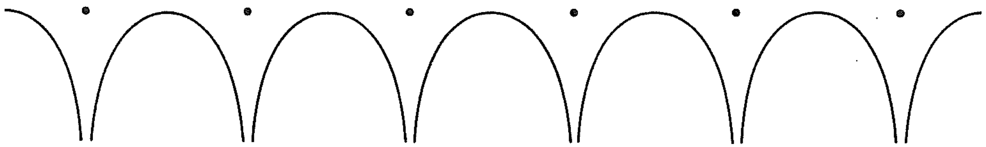
$\Rightarrow |\vec k|$ small $\Rightarrow \frac{2\pi}{\lambda} \ll a$ ← lattice constant

OR $\lambda \gg a$



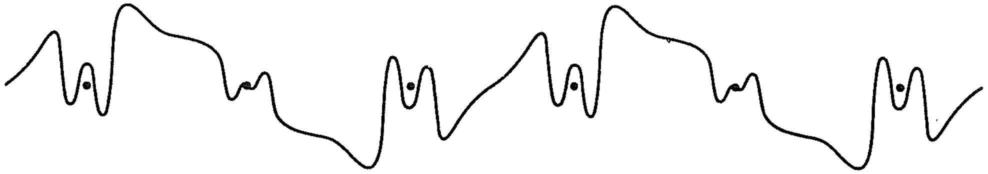
$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r})$$

Potential energy function



(a) $U(\vec{r})$

$$\psi_{\vec{k}}(\vec{r})$$

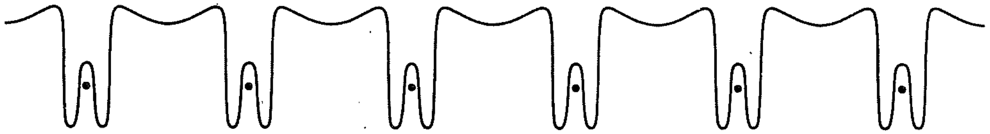


(b) ψ_k

$$\|$$

$$u_{\vec{k}}(\vec{r})$$

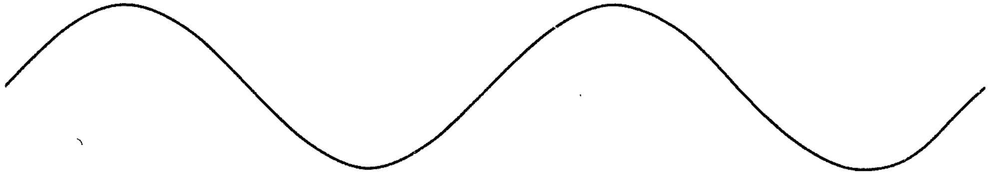
[same period as lattice]



(c) u_k

$$\cdot$$

$$e^{i\vec{k}\cdot\vec{r}}$$



(d) $e^{ik\cdot r}$

A schematic representation of electronic eigenstates in a crystal. (a) The potential plotted along a row of atoms. (b) A sample eigenstate; the state itself is complex but only the real part is shown. This state can be factored into Bloch function (c), which has the periodicity of the lattice, and (d) a plane wave, the real part of which is shown.

Taken from Harrison, "Solid State Theory"

(e) The Band index "n"

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\underbrace{\psi(\vec{r})}_{\sum_{\vec{G}} C_{\vec{k}+\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}}} = E\,\underbrace{\psi(\vec{r})}$$

energy band problem

(for a wavevector $\vec{k}$) ← living in reciprocal space ($\frac{1}{\text{length}}$ space) or $\vec{k}$-space

☞ {One $\vec{k}$ in reciprocal space (e.g. somewhere in 1st B.Z.), equation becomes specific for that $\vec{k}$

Meaning: One $\vec{k}$ ⇒ $\underbrace{\text{a big matrix problem}}$

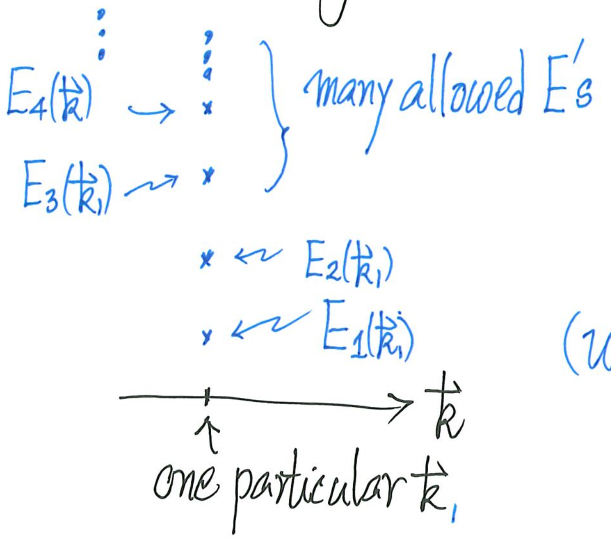
basis functions

$$\left\{e^{i\vec{k}\cdot\vec{r}},\ e^{i(\vec{k}+\vec{G}_1)\cdot\vec{r}},\ e^{i(\vec{k}+\vec{G}_2)\cdot\vec{r}},\ \ldots,\ e^{i(\vec{k}+\vec{G})\cdot\vec{r}},\ \ldots\right\}$$

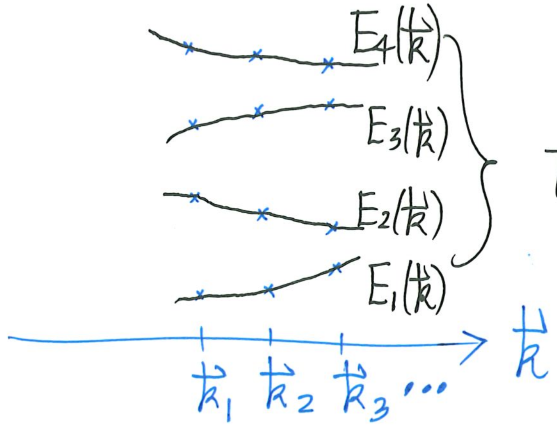
⇓

many allowed energies for that $\vec{k}$

(use an index "n" to label the many allowed energies for the particular $\vec{k}$; thus $E_n(\vec{k})$)



- Repeat process for many different wavevectors $\vec{k}$'s



these give the electronic energy bands

$$\underbrace{E_n(\vec{k})}_{\text{more popular}} \quad \text{or} \quad \underbrace{E_{n\vec{k}}}_{\text{perfectly right!}}$$

Therefore, $\psi_{n\vec{k}}(\vec{r}) \longleftrightarrow E_n(\vec{k})$ (TISE gives many many pairs)

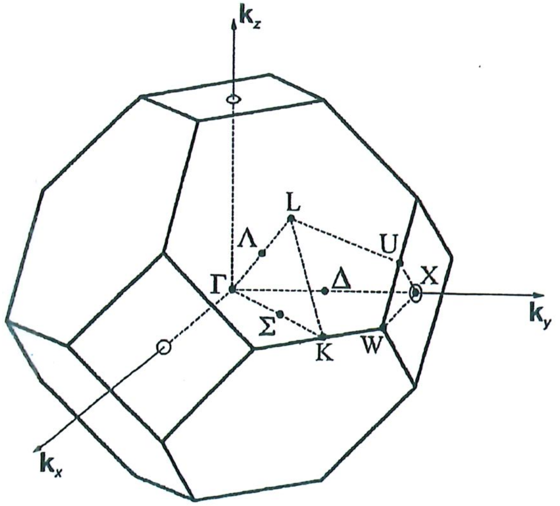
Bloch form

band index   band index

[energy eigenstates] [energy eigenvalues]

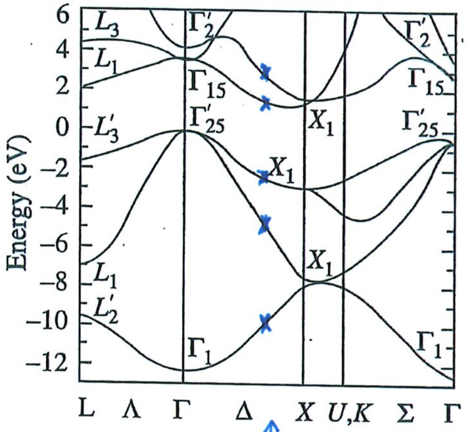
Bloch functions

This subsection states a general approach of solving the energy band problem.



1st B.Z.

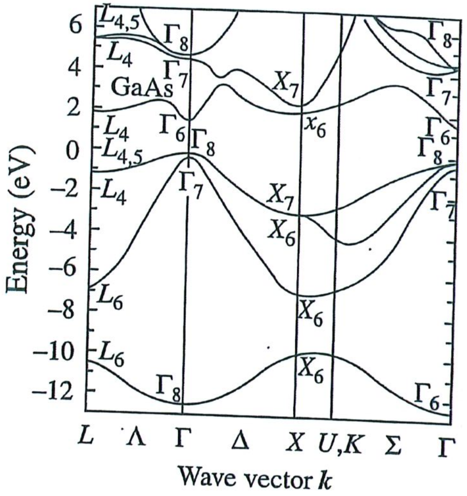
Silicon



[one k, many energies]

Band structure of Si (after Chelikowsky and Cohen 1976).

GaAs



Band structure of GaAs (after Chelikowsky and Cohen 1976).

"Δ" : a line from Γ to X

x-axis: trace some paths in B.Z
(line to edge (zone edge) and back)

∴ Bloch Functions are solutions to TISE (with periodic $U(\vec{r})$) and they have the forms

$$\psi_{n\vec{k}}(\vec{r}+\vec{R}_i) = e^{i\vec{k}\cdot\vec{R}_i}\,\psi_{n\vec{k}}(\vec{r}) \qquad 14)$$

$\{\vec{R}_i\}$ lattice constants

OR

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\,u_{n\vec{k}}(\vec{r}) \quad \text{with} \quad u_{n\vec{k}}(\vec{r}+\vec{R}_i) = u_{n\vec{k}}(\vec{r}) \qquad (15)$$

(up to a normalization constant)

They can also be written as

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{n,\vec{k}+\vec{G}}\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \qquad (16)$$