Lecture 1

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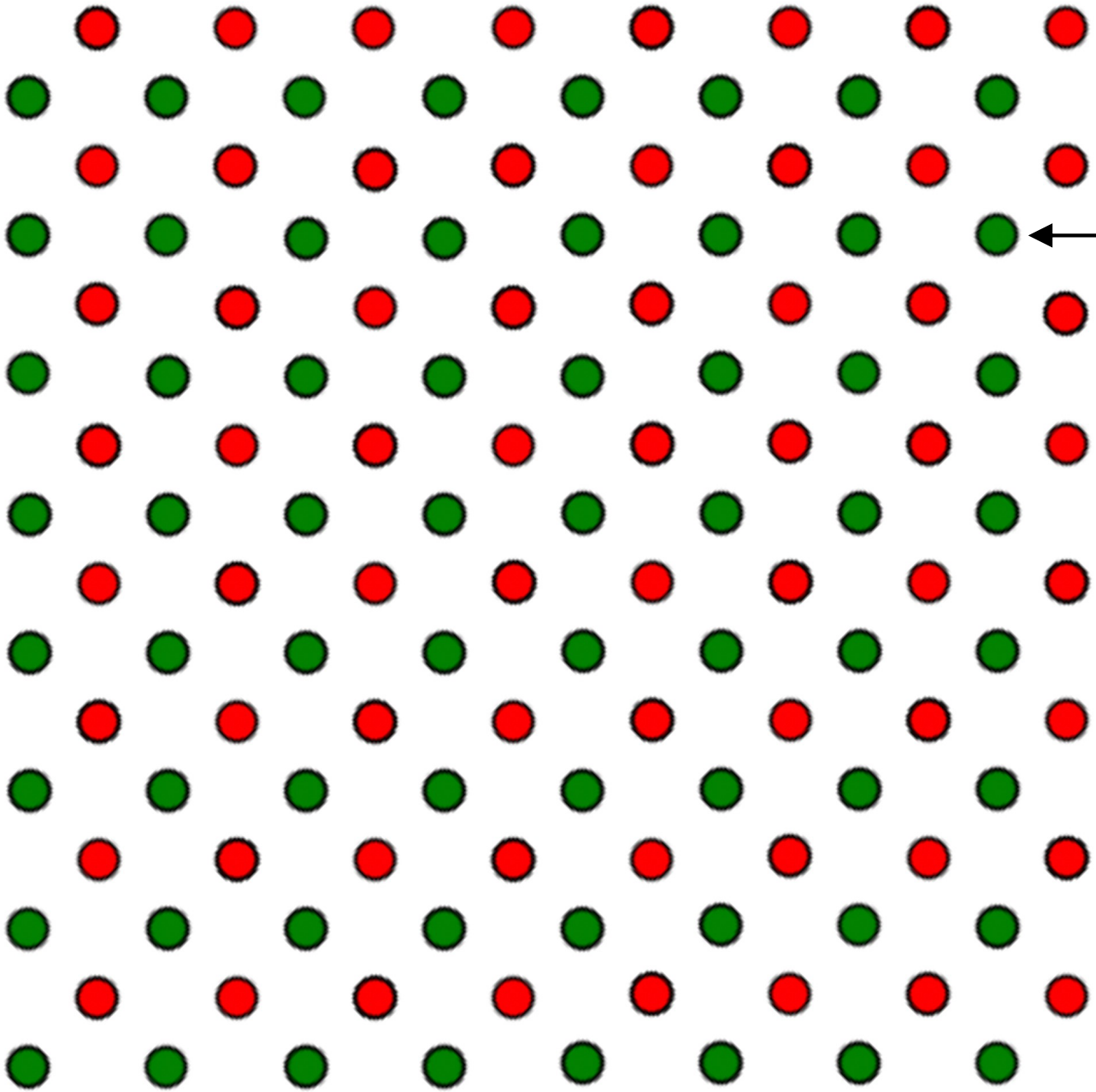
TYC Oct 2024

Crystal Structure: Materials

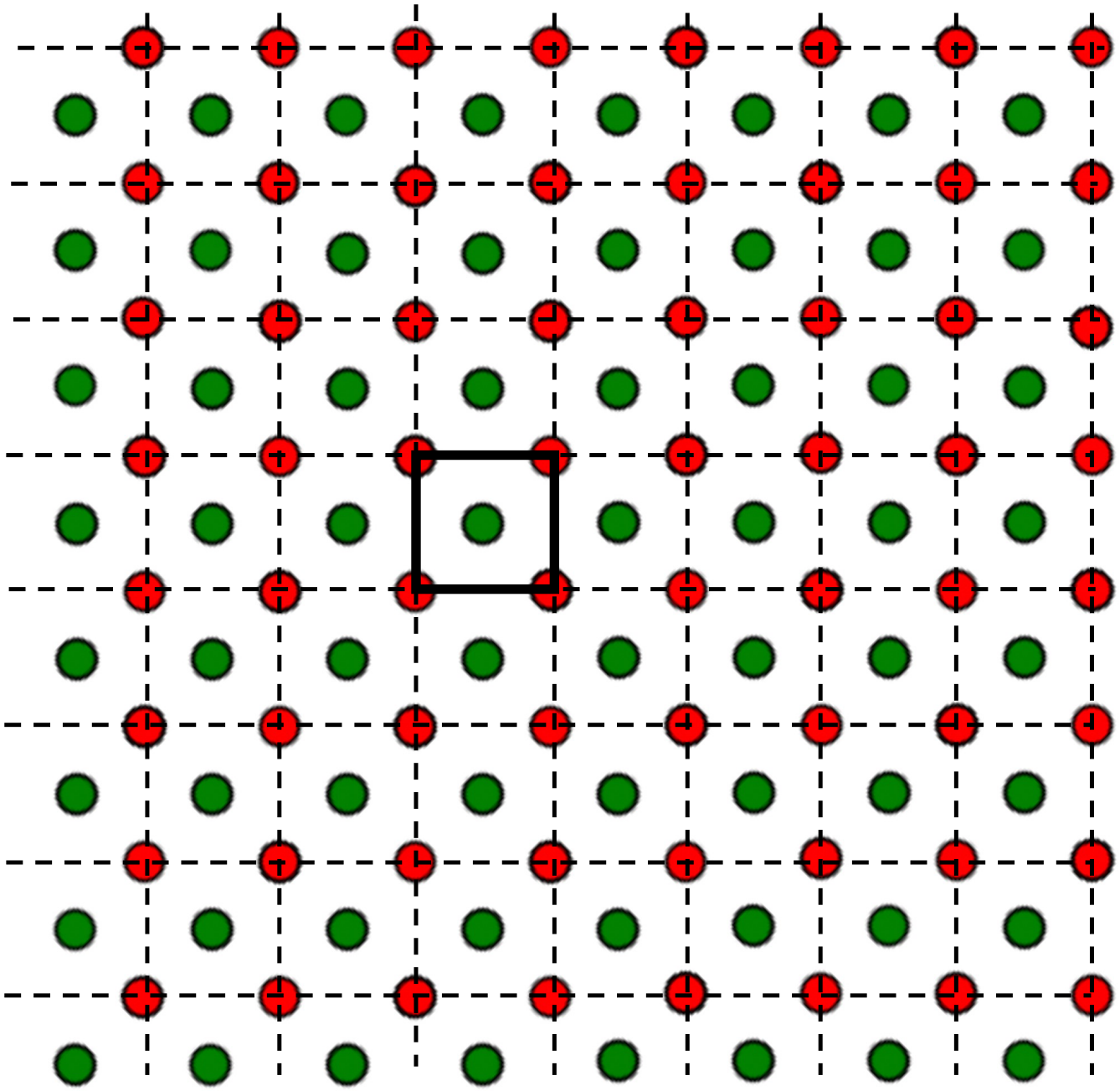


Ex: "MgO"

e.g. Mg

e.g. O

Crystal Structure: Periodic Repeating



"Unit cell"

"Smallest Repeating Pattern"

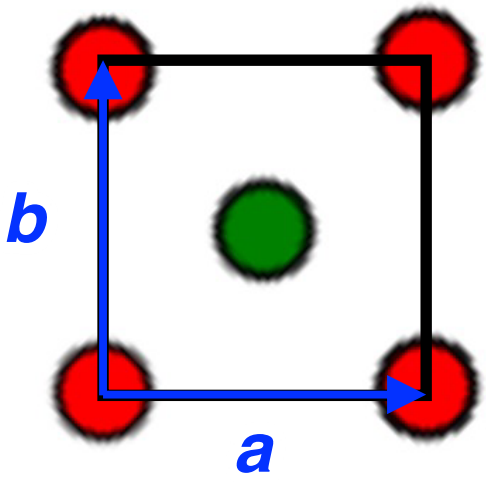
Can be composed of one, two, or many atomic species (depends on material)

Crystal Structure: Unit Cell

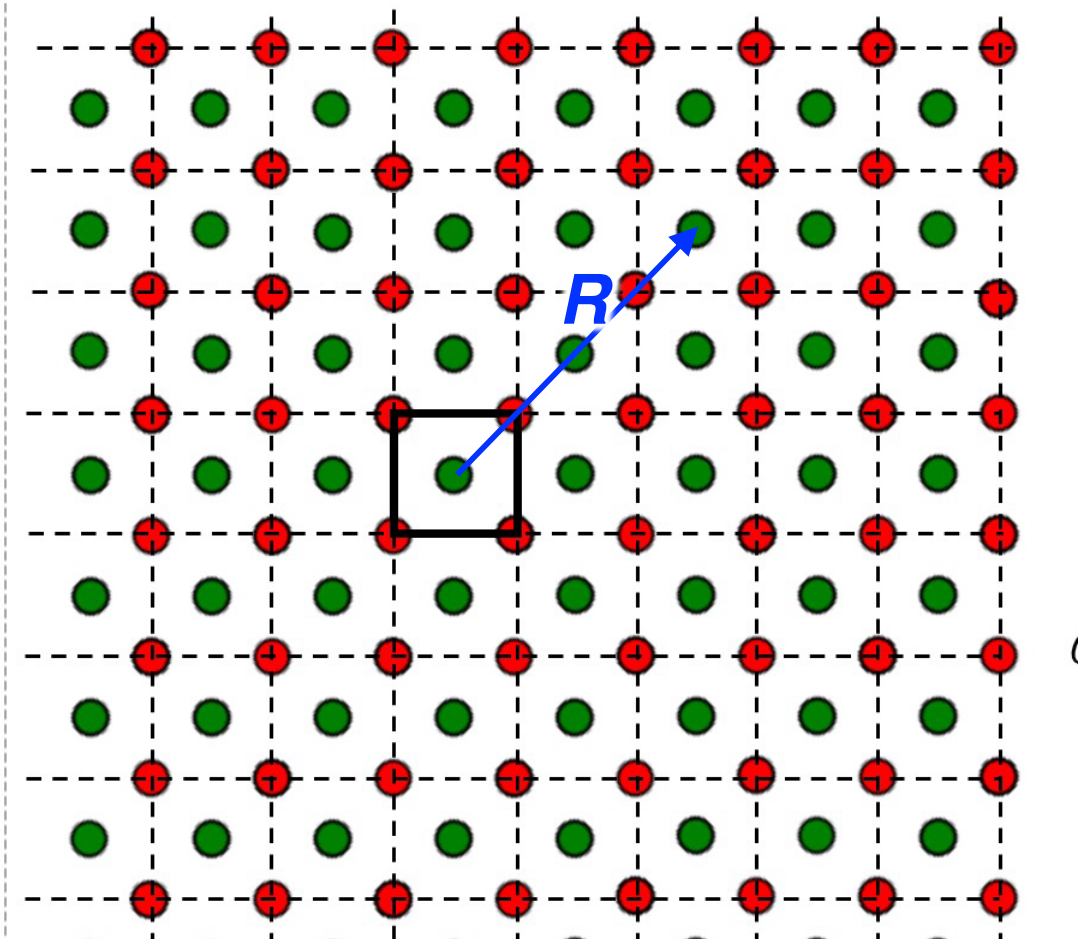
=> The shape and translation of a unit cell are determined by its unit vectors…

- *2D: (**a**,**b**)* ← *Notation: Bold font used for vectors*
- *3D: (**a**,**b**,**c**) (e.g., out of the plane below)*

=> Translation vector: $\mathbf{R}=n_a\mathbf{a}+n_b\mathbf{b}+n_c\mathbf{c}$ *(integers:* n_a, n_a, n_c*)*

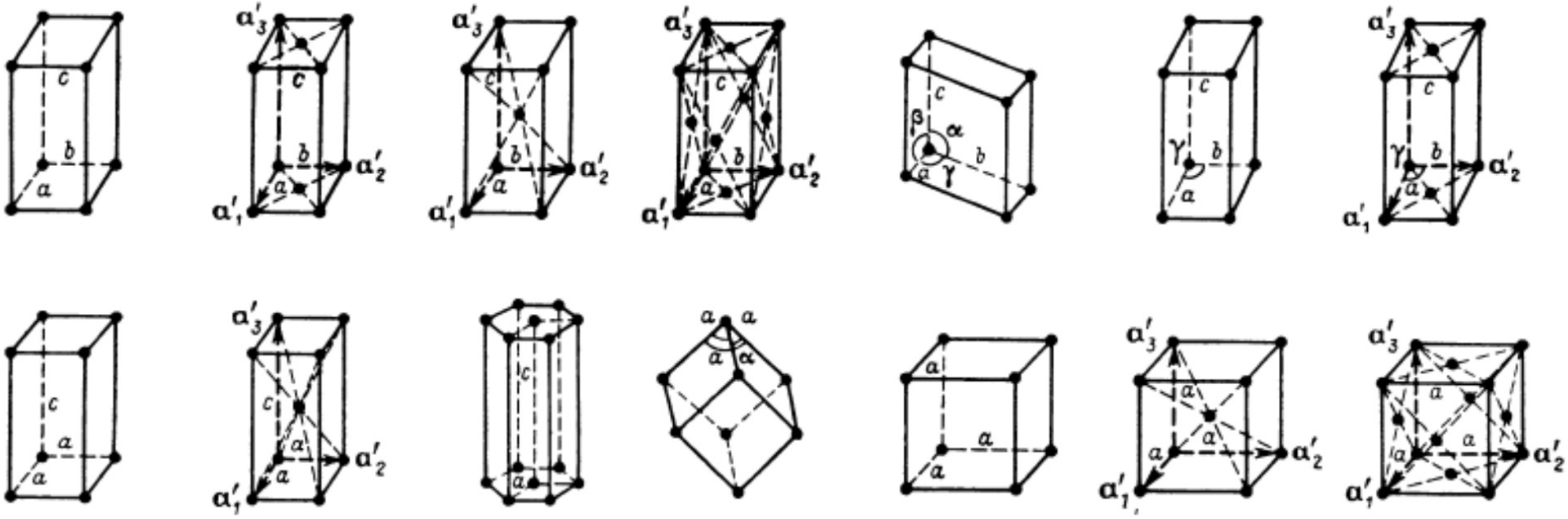


Unit Cell



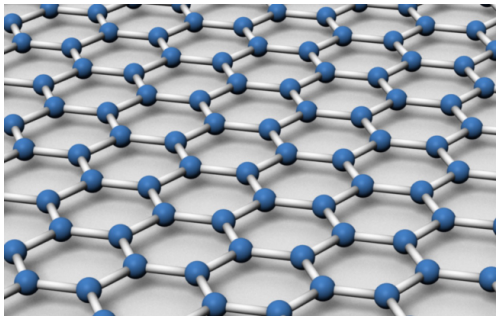
Crystal Structure: Unit Cells 3D

=> Bravais lattices form the general classification of material unit cells in 3D…14 total…



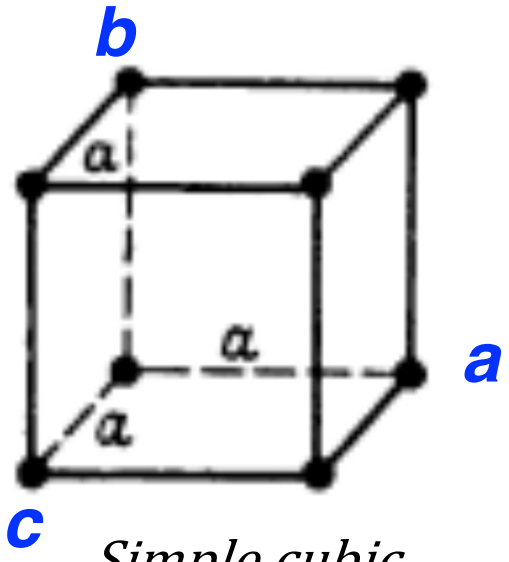
…There are also 2D Bravais lattices (e.g., graphene & boron nitride). Further details:

https://en.wikipedia.org/wiki/Bravais_lattice



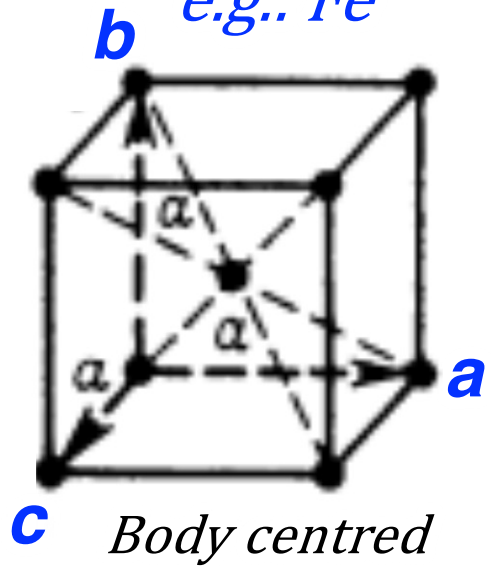
Crystal Structure: Unit Cells 3D

=> Some common lattices in materials (cubic group: a=b=c)...



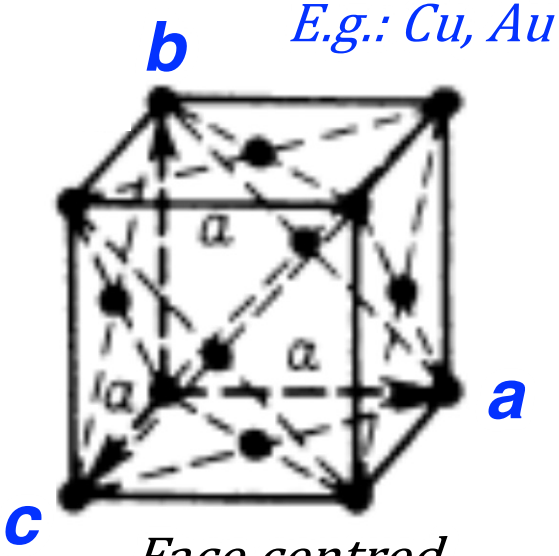
Simple cubic

e.g.: Fe



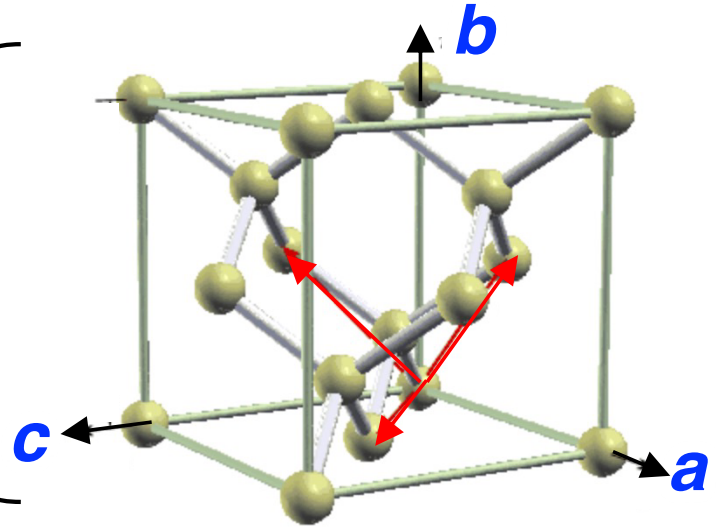
Body centred Cubic (BCC)

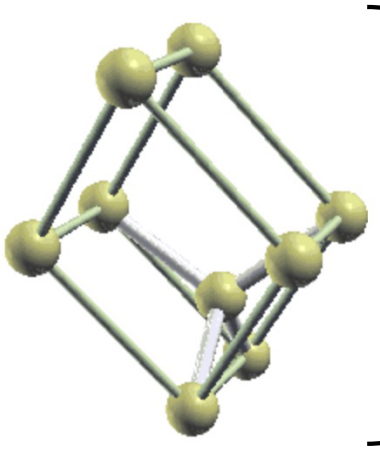
E.g.: Cu, Au



Face centred Cubic (FCC)

conventional cubic diamond unit cell

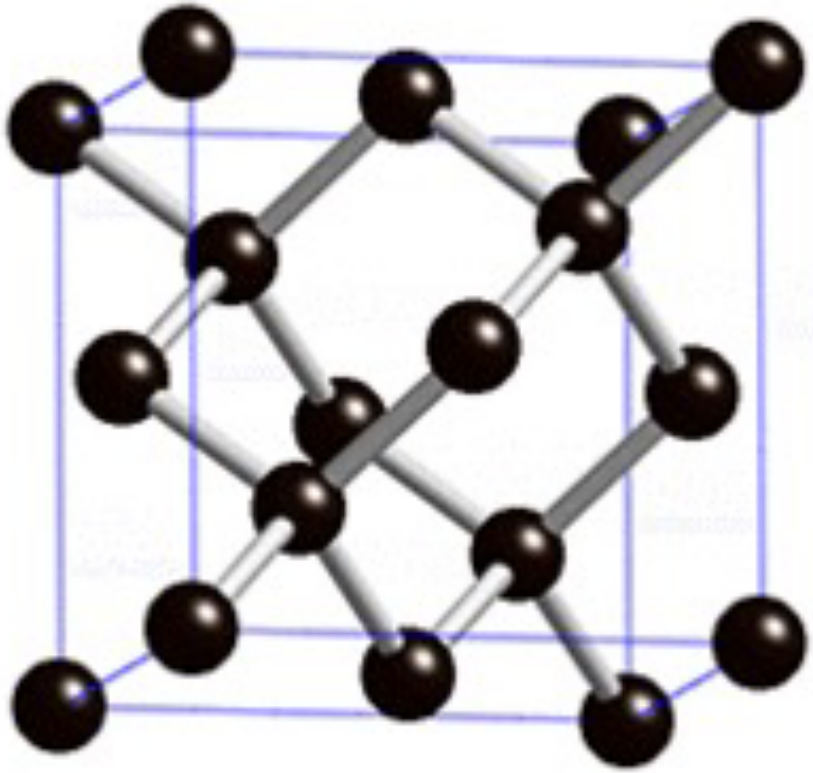


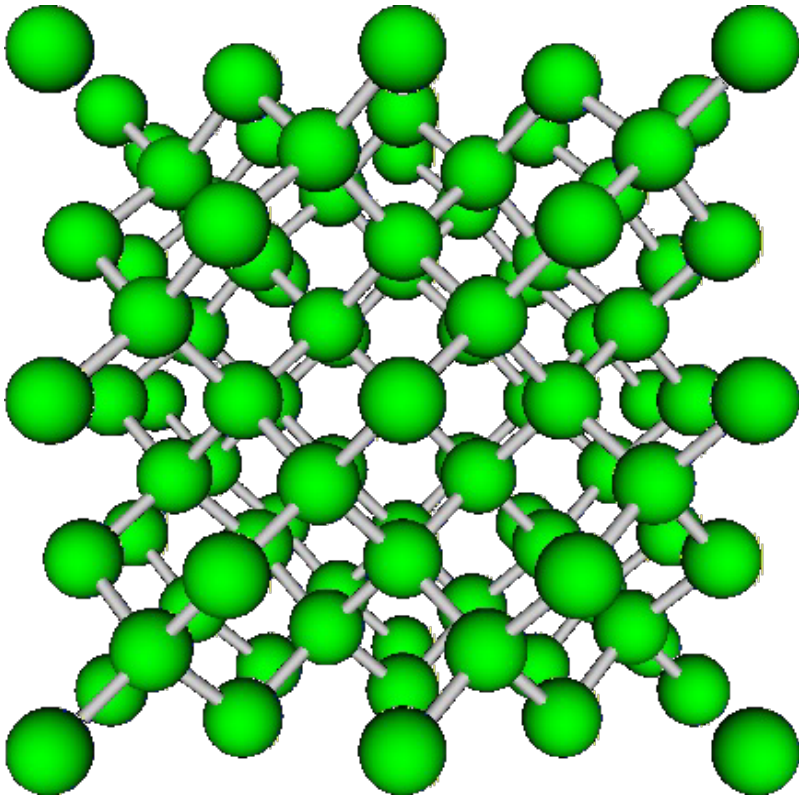


primitive diamond unit cell (important for electronic properties)

Crystal Structure: Diamond Lattice

=> Silicon is the primary electronic material...

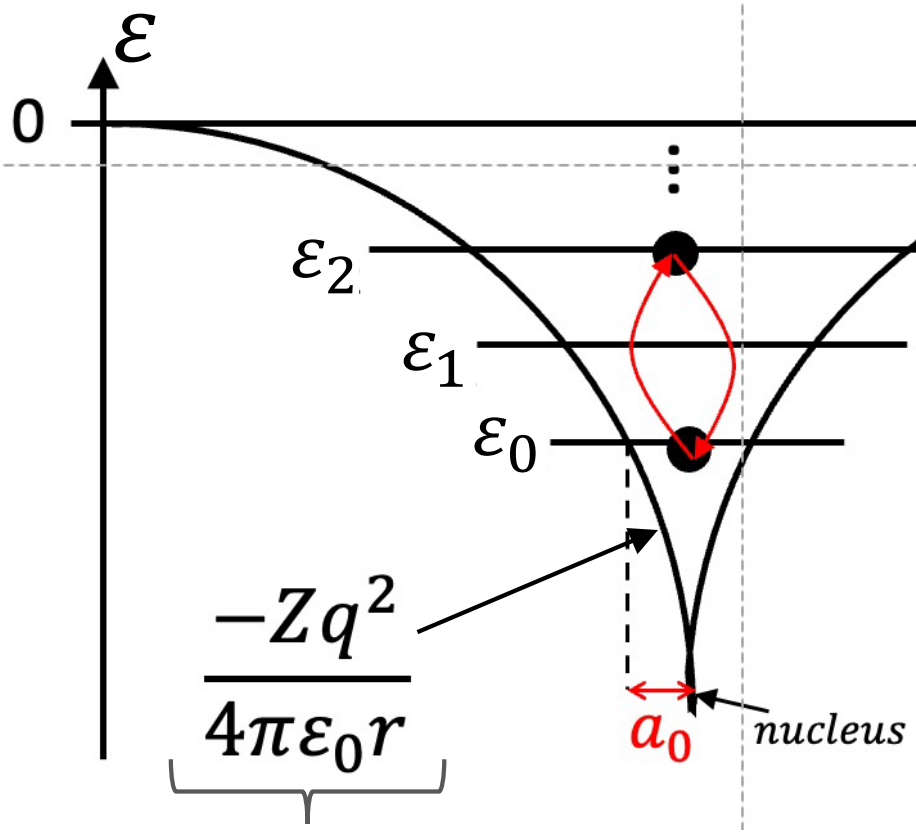




"electronic structure" ↔ "atomic structure"

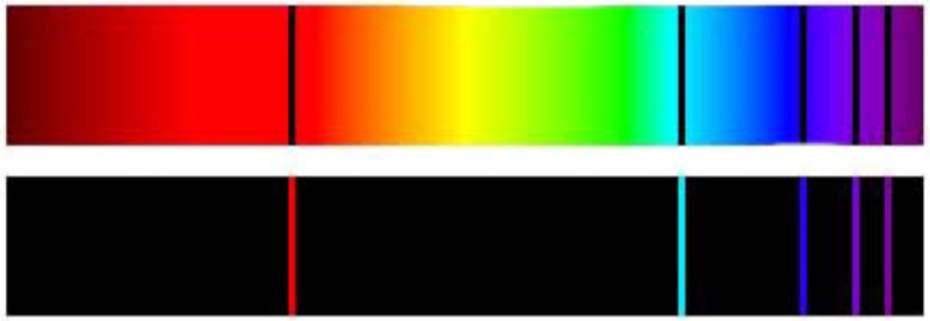
Atoms & Electrons

=> Take just one atom (e.g., hydrogen via the Bohr model)...



ε_0=-13.6 eV

$$\hbar\omega = \varepsilon_\beta - \varepsilon_\alpha = Z^2\left(\frac{1}{\alpha^2} - \frac{1}{\beta^2}\right)\varepsilon_0$$

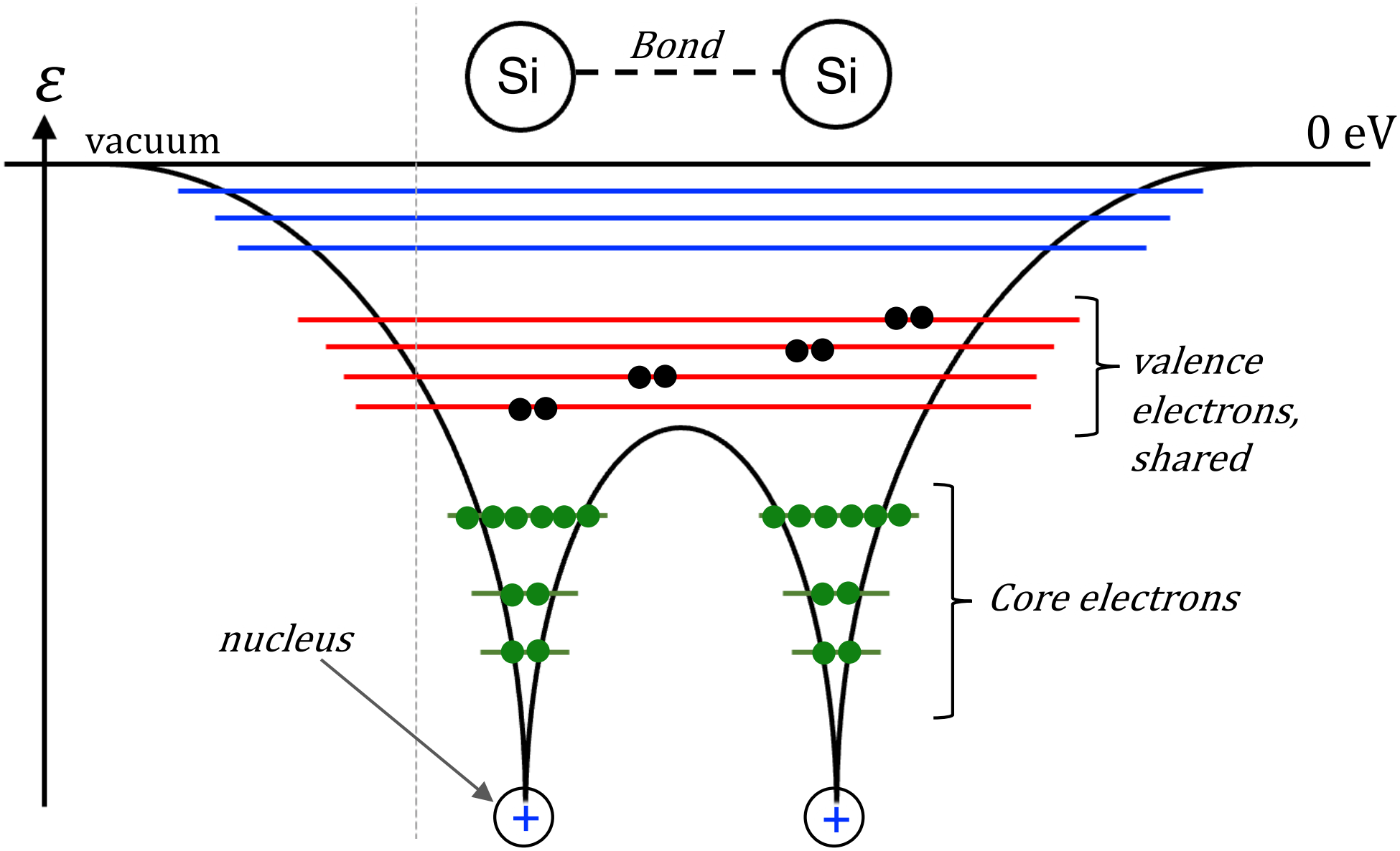


Nuclear potential, Z=1 for hydrogen

=> Electrons are bound below 0 eV (vacuum reference), transition between discrete energy levels.

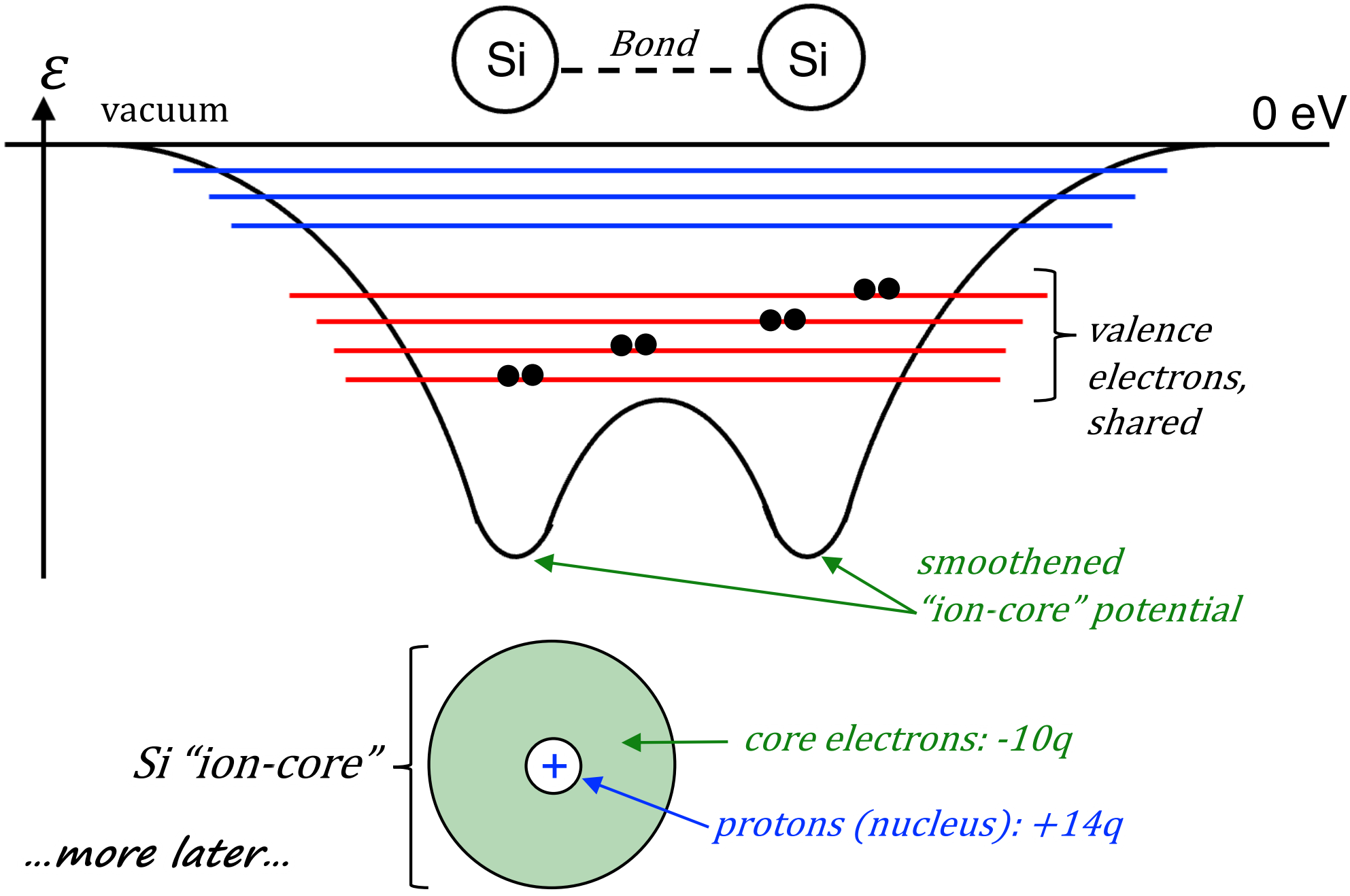
=> What happens in a material (crystal)?

First Two Si Atoms ("Molecule")



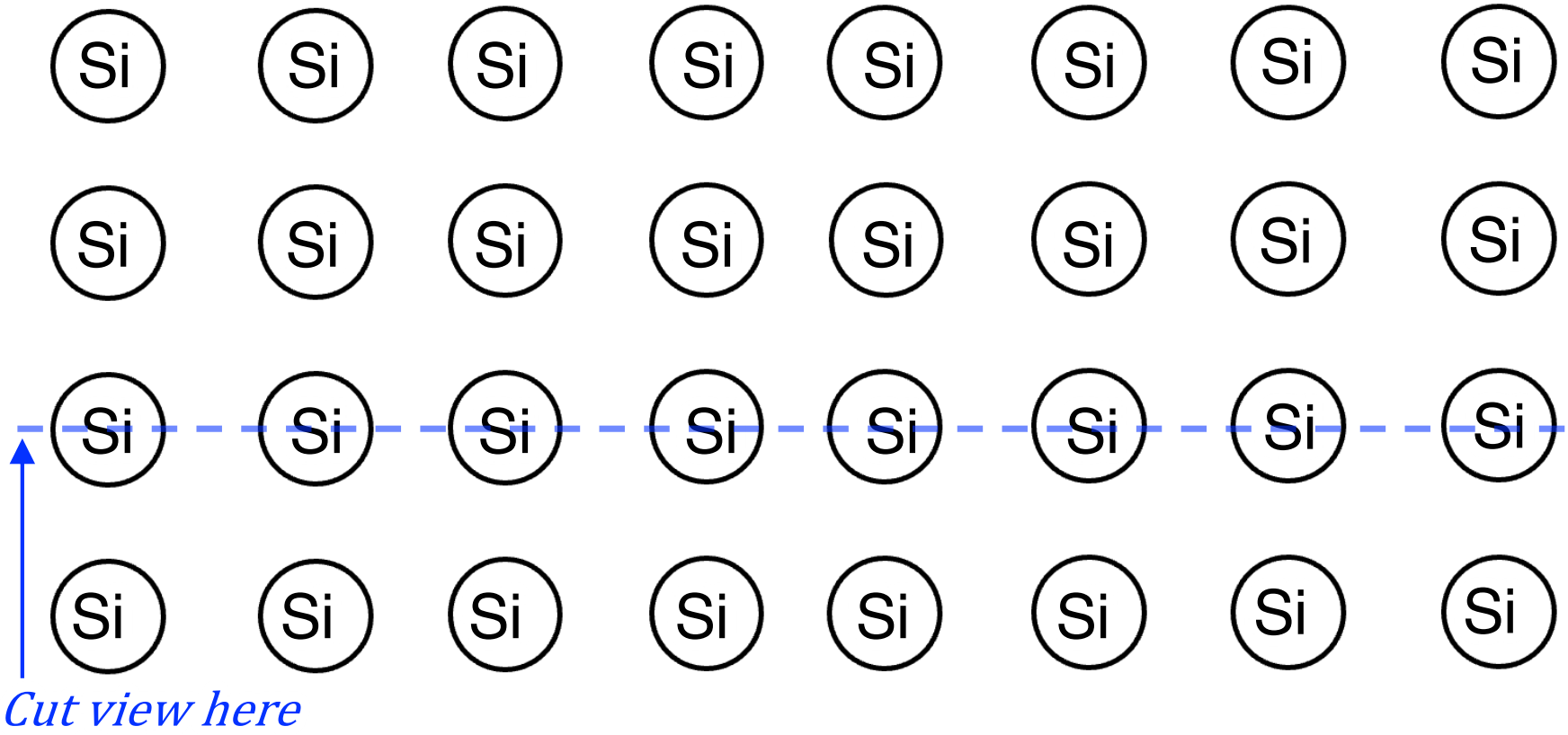
=> Electrons are still bound below 0 eV (vacuum reference).

"Ion-Core" Concept ("Ignore" Core Electrons)



Crystals & Electrons

=> Repeat many atoms, via a unit cell, leads to many repeating (ion-core) potential wells... e.g., silicon (simplified view)...

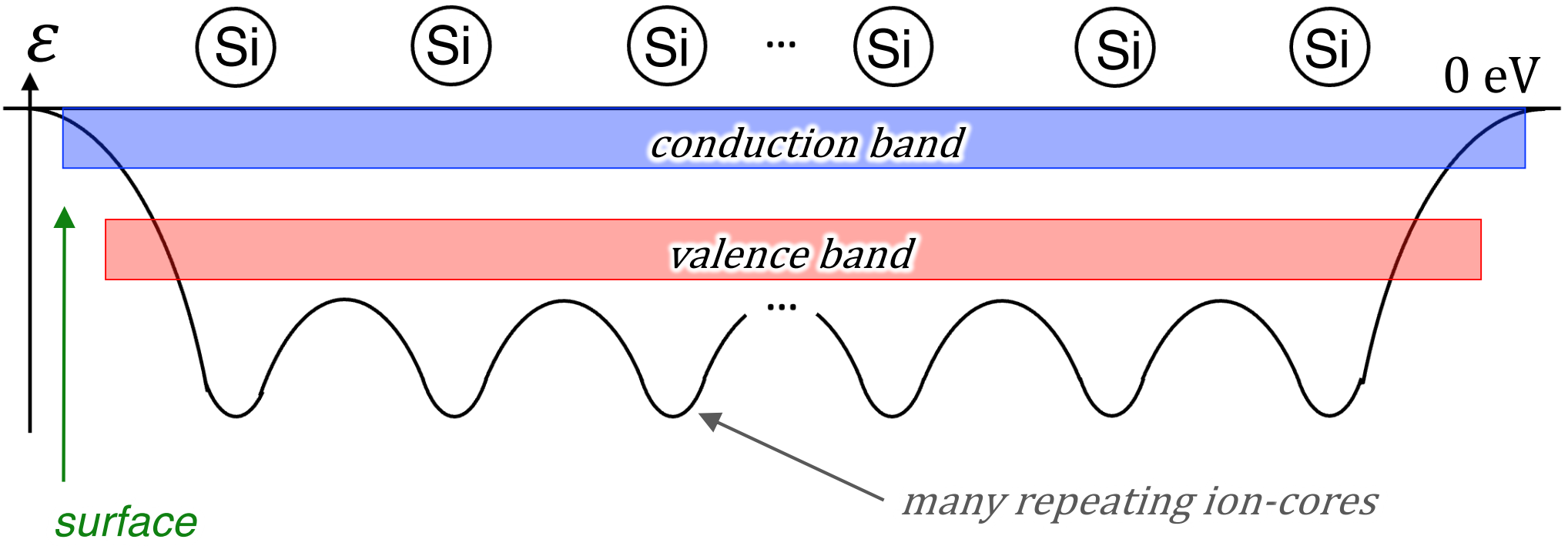


=> What does this mean for the electrons?....

=> Electrons are still bound below 0 eV (vacuum reference).

Crystals & Electrons: Repeating Wells

=> Repeat many atoms, via a unit cell, leads to many repeating (ion-core) potential wells... e.g., silicon with surface...

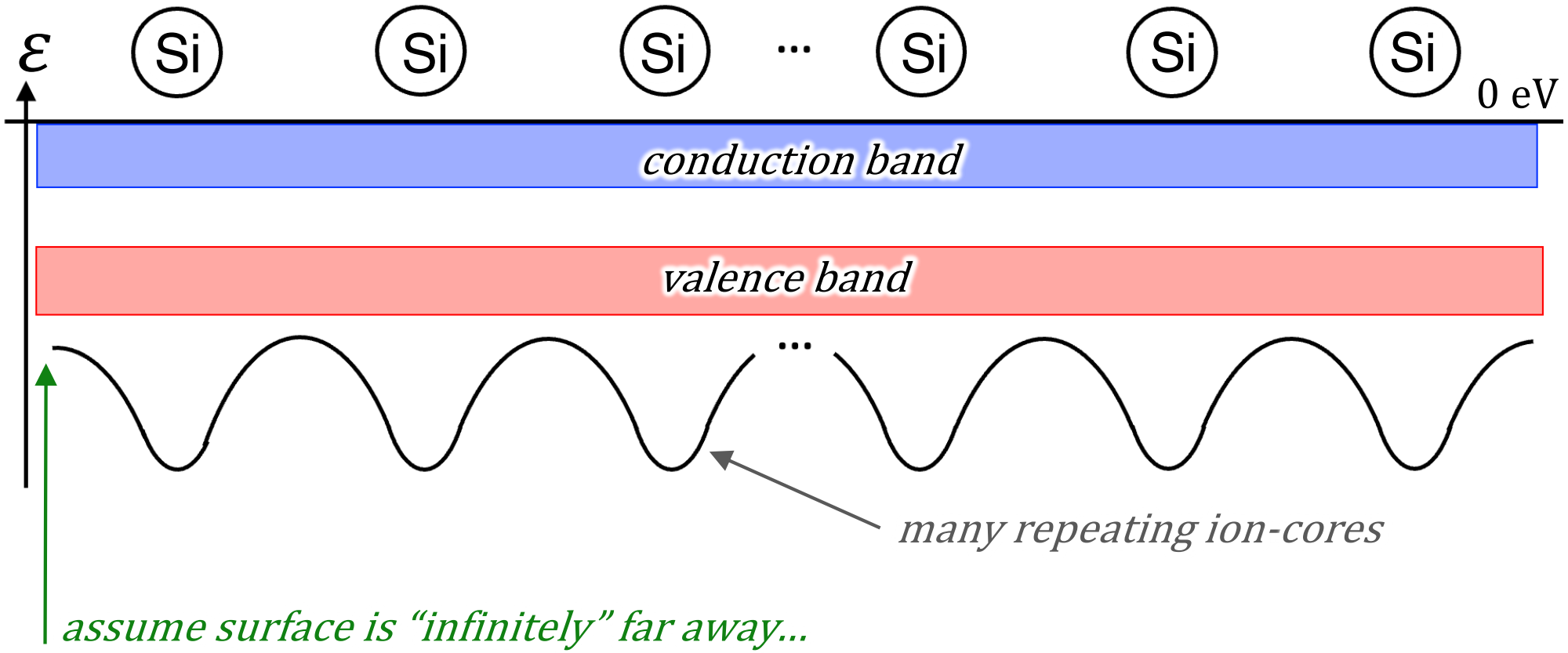


=> What does this mean for the electrons?....

=> Electrons are still bound below 0 eV (vacuum reference).

Crystals & Electrons

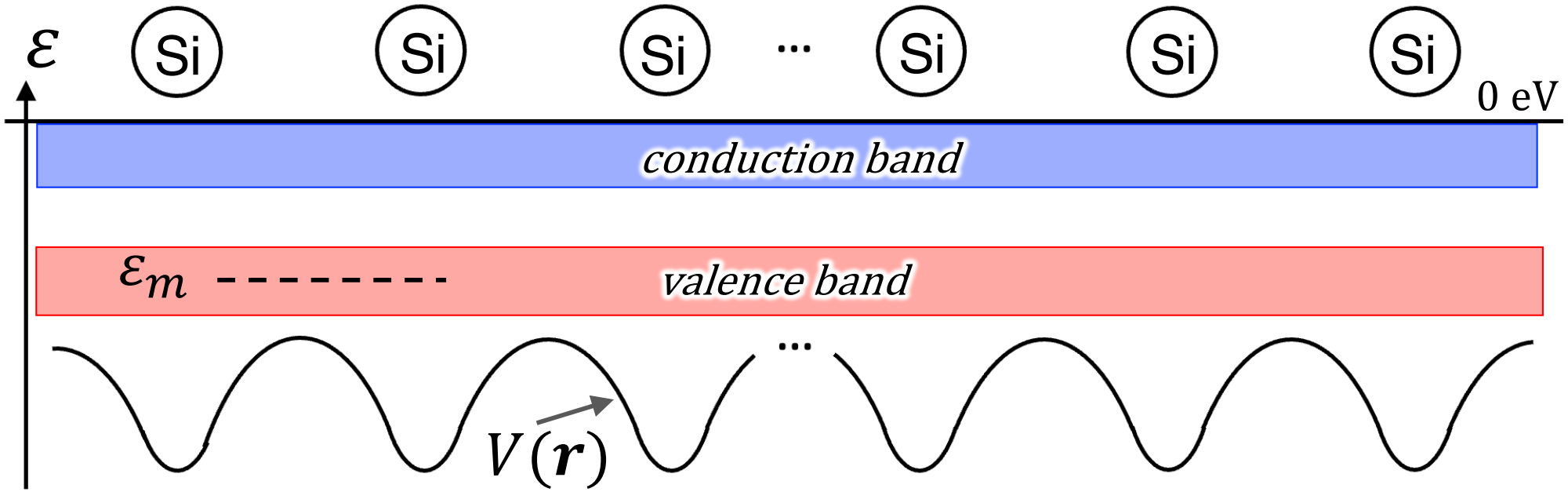
=> Repeat many atoms, via a unit cell, leads to many repeating (ion-core) potential wells... e.g., silicon "without" surface...



=> "Infinite" lattice... what does this mean for the electrons?....

=> Electrons are still bound below 0 eV (vacuum reference).

Crystals & Electrons: Quantum



=> Consequences for electrons are determined by Quantum Mechanics?.... (using the Kohn-Sham equation)...

wavefunction

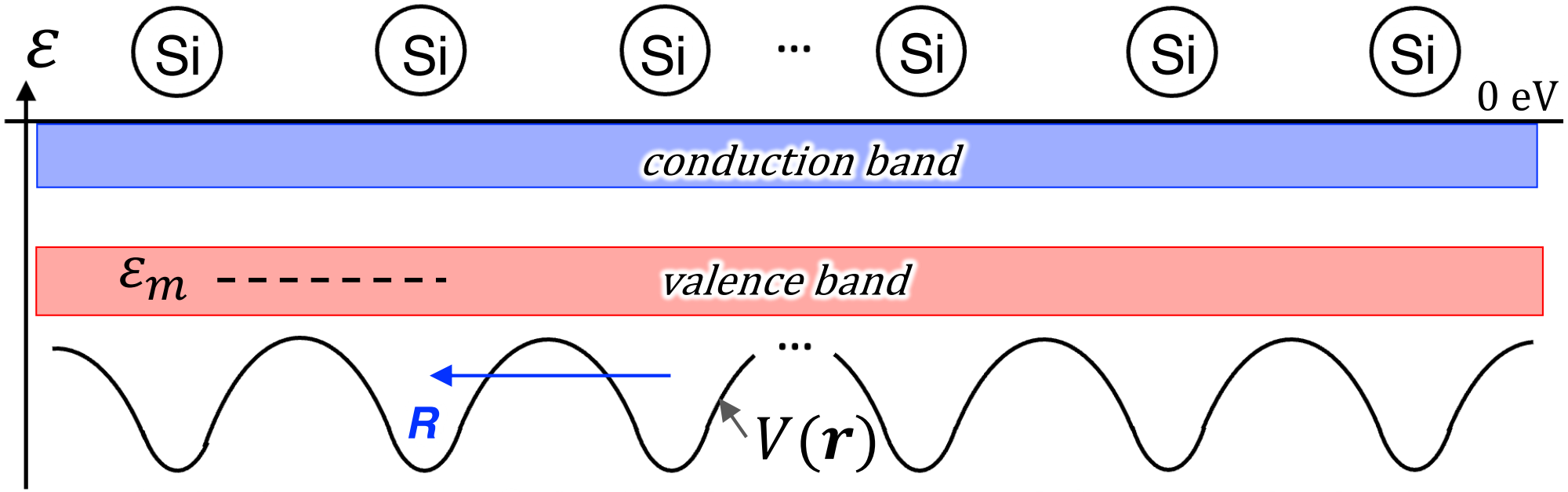
kinetic

$$\varepsilon_m \psi_m = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\boldsymbol{r}) \right] \psi_m$$

energy level (e.g., in a "band")

potential

Crystals & Electrons: Quantum



=> Bloch theorem: "If the lattice and potential are periodic then the electron density for each wavefunction of that lattice must be be so also..."

$$\varepsilon_m \psi_m = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\boldsymbol{r}) \right] \psi_m$$

$$V(\boldsymbol{r} + \boldsymbol{R}) = V(\boldsymbol{r})$$

$$\therefore \quad \rho_m(\boldsymbol{r} + \boldsymbol{R}) = \rho_m(\boldsymbol{r})$$

$$\rho_m(\boldsymbol{r}) = \psi_m \psi_m^*$$

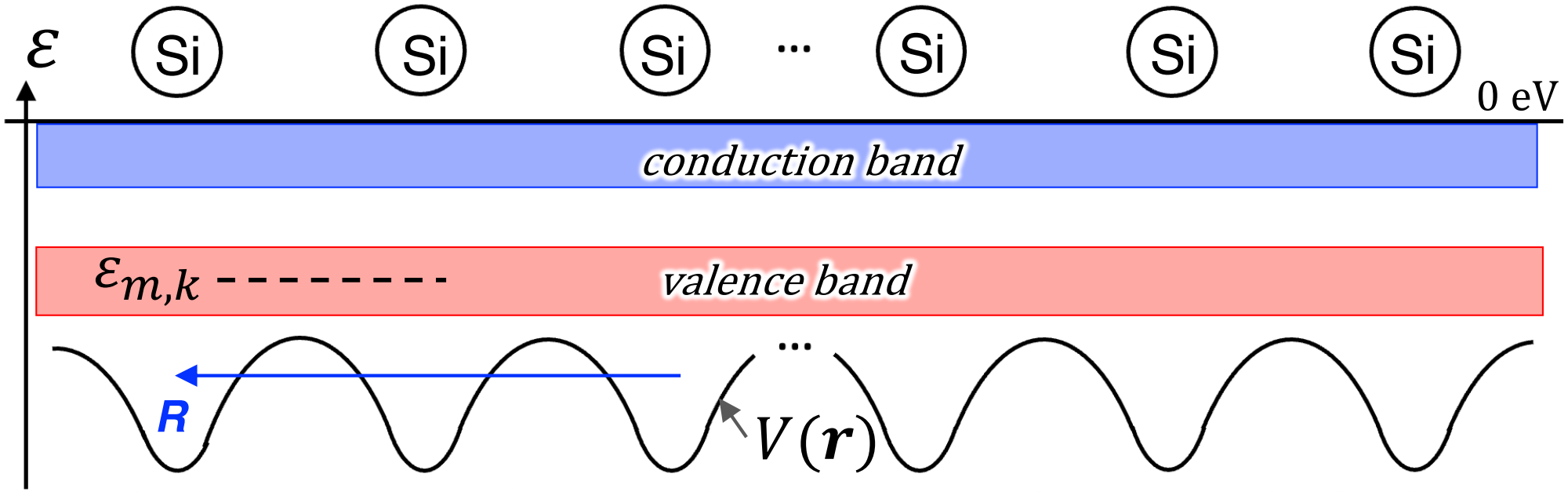
$$\therefore \psi_m(\boldsymbol{r}) \psi_m^*(\boldsymbol{r})$$

$$= \psi_m(\boldsymbol{r} + \boldsymbol{R}) \psi_m^*(\boldsymbol{r} + \boldsymbol{R})$$

$$= e^{i\phi} \psi_m(\boldsymbol{r}) e^{-i\phi} \psi_m^*(\boldsymbol{r})$$

phase

Crystals & Electrons: Quantum



=> Bloch theorem: "If the lattice and potential are periodic then the electron density for each wavefunction of that lattice must be be so also…"

$$\varepsilon_{m,k}\psi_{m,k} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi_{m,k}$$

new "k" index

$$\psi_{m,k}(\boldsymbol{r}+\boldsymbol{R}) = e^{+i\phi}\,\psi_{m,k}(\boldsymbol{r})$$

Let: $\phi = \boldsymbol{k}\cdot\boldsymbol{R}$

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

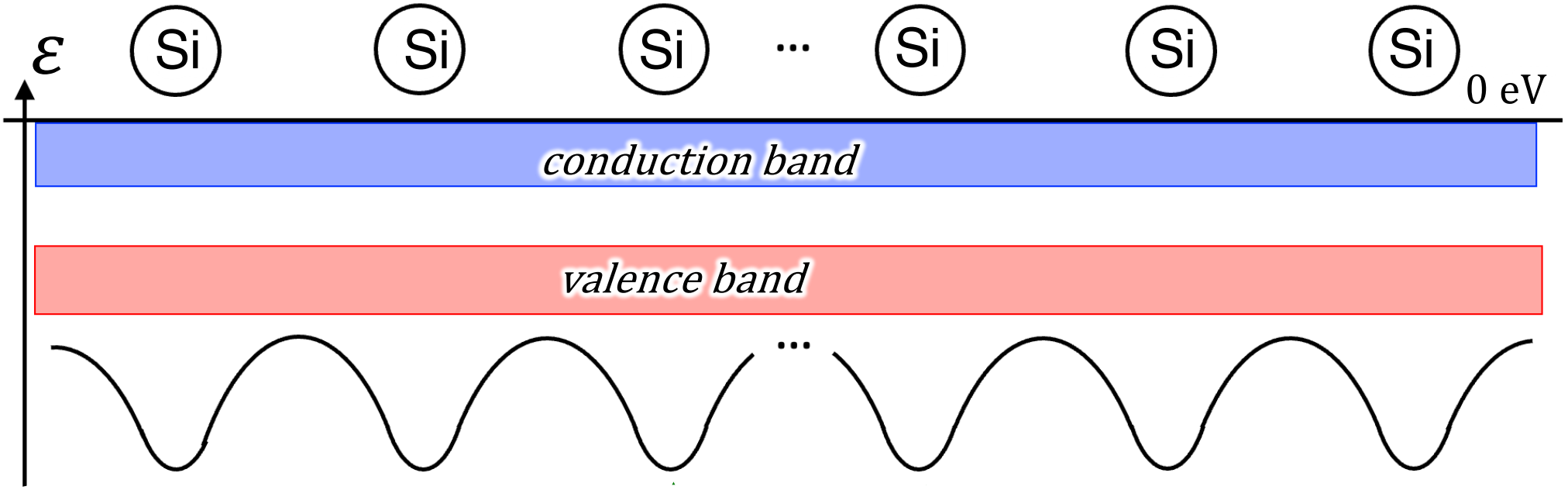
$$\underbrace{u_{m,k}(\boldsymbol{r}+\boldsymbol{R}) = u_{m,k}(\boldsymbol{r})}$$

periodic Bloch wave

=> What is k?

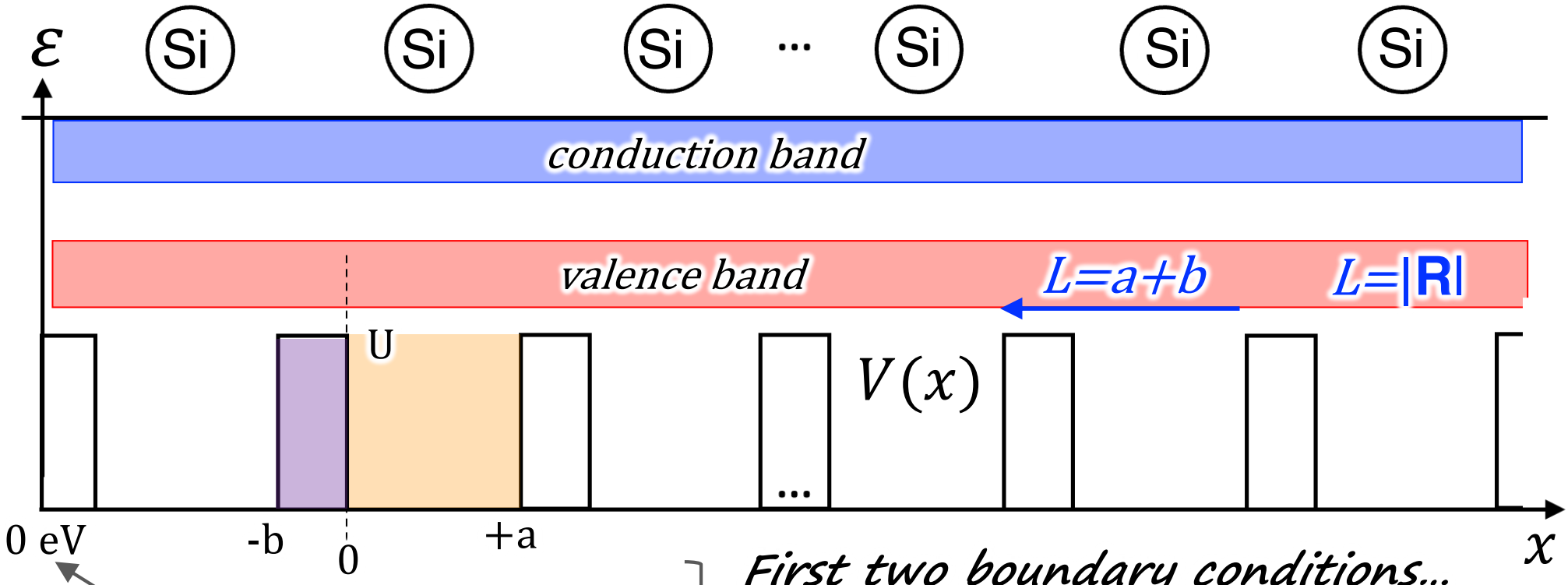
Crystals & Electrons: Quantum

=> Let us use periodically repeating "square wells", rather than rounded wells, to work out analytically what "k" means...



Crystals & Electrons: Quantum

=> Let us use periodically repeating "square wells", rather than rounded wells, to work out analytically what "k" means...



shift reference, simplifies algebra...

$$\varepsilon\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi$$

drop indices for now...

First two boundary conditions...

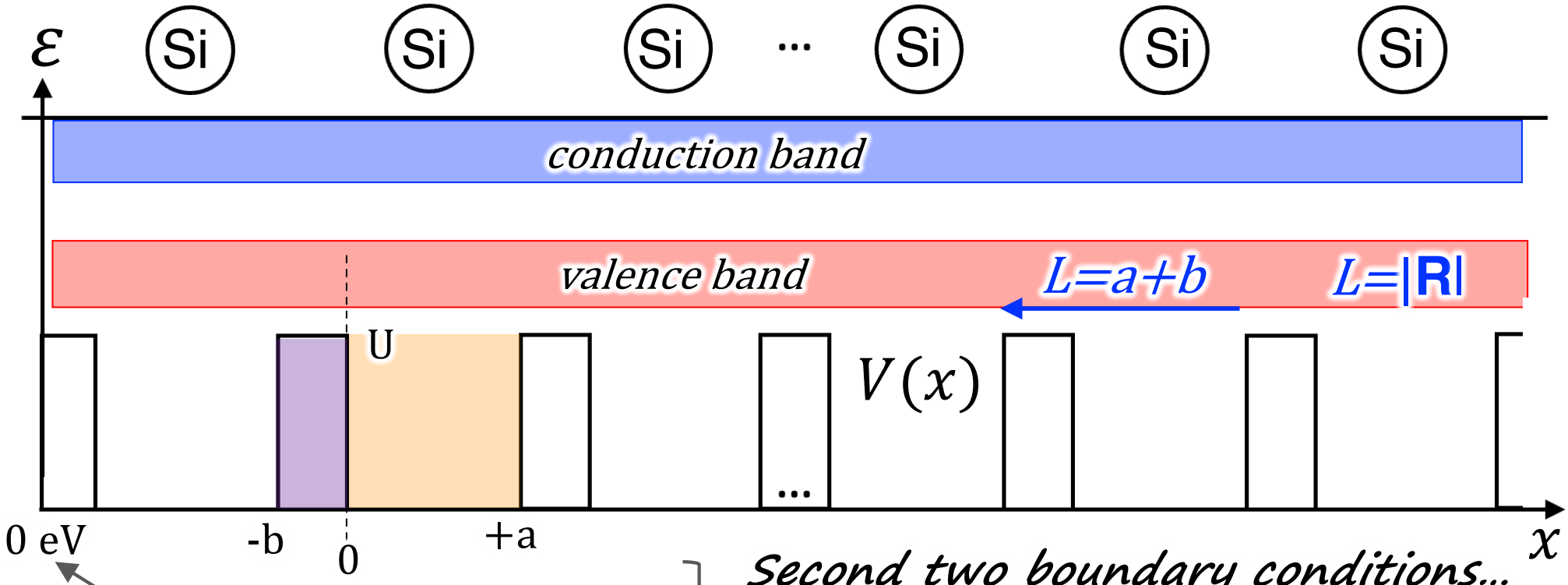
$$\psi(x=0) = \psi(x=0)$$

$$\psi(x=+a) = e^{ikL}\psi(x=-b)$$

k-value!

Crystals & Electrons: Quantum

=> Let us use periodically repeating "square wells", rather than rounded wells, to work out analytically what "k" means...



shift reference, simplifies algebra...

$$\varepsilon\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi$$

drop "m" index for now...

Second two boundary conditions...

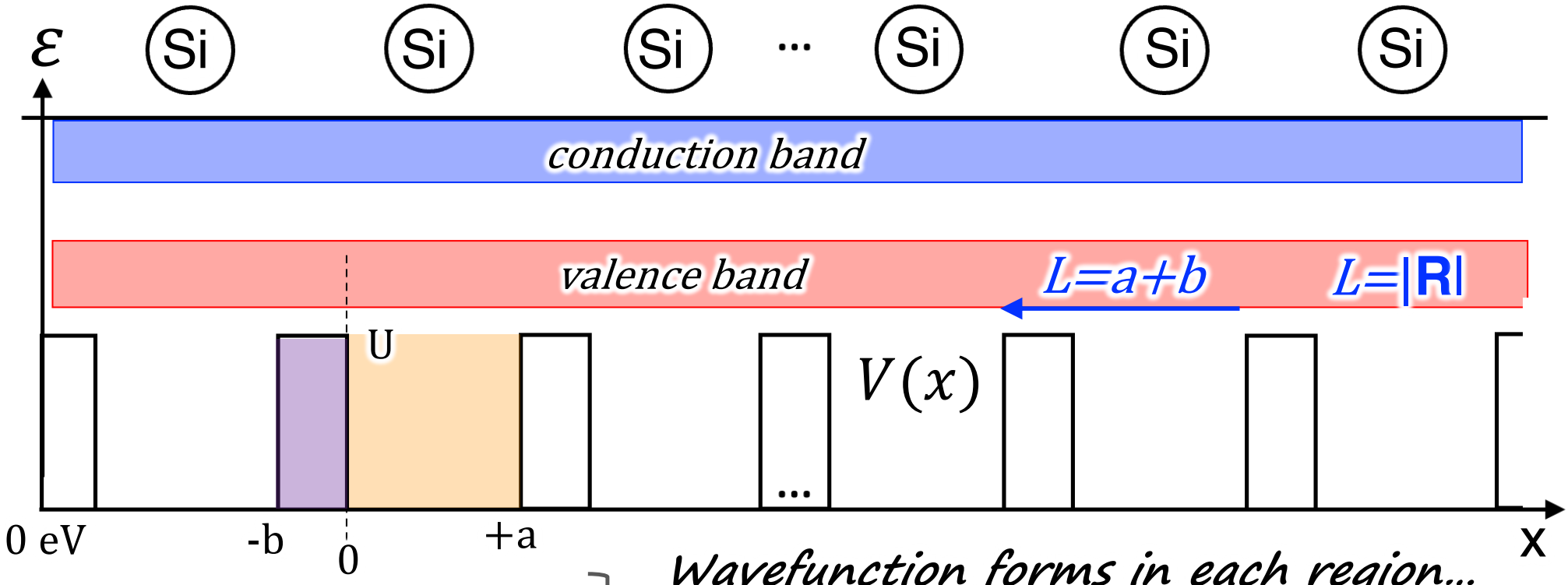
$$\left[\frac{d\psi}{dx}\right]_{x=0} = \left[\frac{d\psi}{dx}\right]_{x=0}$$

$$\left[\frac{d\psi}{dx}\right]_{x=+a} = e^{ikL}\left[\frac{d\psi}{dx}\right]_{x=-b}$$

k-value!

Crystals & Electrons: Quantum

=> Let us use periodically repeating "square wells", rather than rounded wells, to work out analytically what "k" means...



$$\varepsilon\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi$$

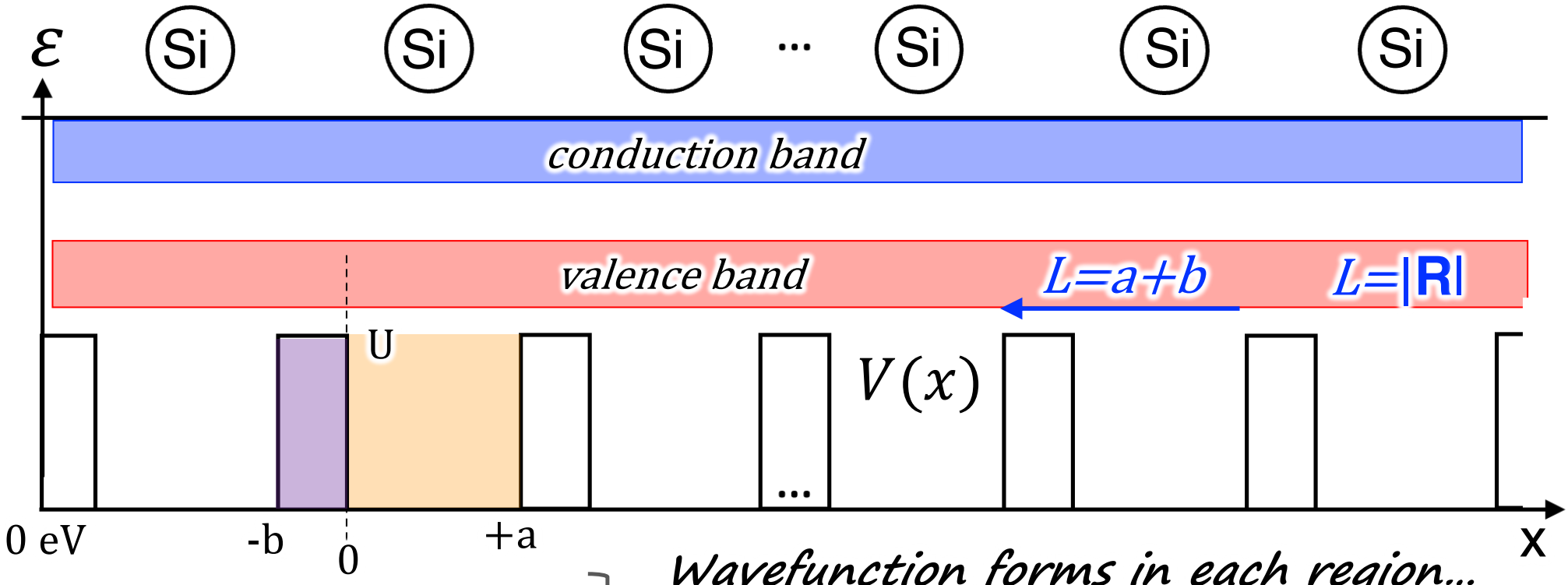
Wavefunction forms in each region...

$$\frac{d^2\psi}{dx^2} = -\gamma^2\,\psi \qquad \gamma = \frac{\sqrt{2m\varepsilon}}{\hbar}$$

$$\psi = Ae^{+i\gamma x} + Be^{-i\gamma x}$$

Crystals & Electrons: Quantum

=> Let us use periodically repeating "square wells", rather than rounded wells, to work out analytically what "k" means...



$$\varepsilon\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi$$

Wavefunction forms in each region...

$$\frac{d^2\psi}{dx^2} = +\beta^2\,\psi \qquad \boxed{\beta = \frac{\sqrt{2m(U-\varepsilon)}}{\hbar}}$$

$$\psi = Ce^{+\beta x} + De^{-\beta x}$$

Crystals & Electrons: Quantum

=> Applying the four boundary conditions to the wavefunctions in each region we obtain four equations and four unknowns...

$$\underbrace{\begin{bmatrix} 1 & 1 & -1 & -1 \\ +i\gamma & -i\gamma & -\beta & +\beta \\ e^{+i\gamma a} & e^{-i\gamma a} & -e^{ikL}e^{-\beta b} & -e^{ikL}e^{+\beta b} \\ +i\gamma e^{+i\gamma a} & -i\gamma e^{-i\gamma a} & -\beta e^{ikL}e^{-\beta b} & \beta e^{ikL}e^{+\beta b} \end{bmatrix}}_{[M]} \underbrace{\begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix}}_{\{v\}} = 0$$

=> No unique solution of A, B, C & D to... $[M]\{v\} = 0$

$$\therefore det[M] = 0$$

=> Alternative not physical....

A=0, B=0, C=0 & D=0 $\quad \therefore \psi = 0$

Crystals & Electrons: Quantum

=> Solving the relation $\det[M] = 0$ *provides...*

$$\beta = \frac{\sqrt{2m(U-\varepsilon)}}{\hbar} \qquad \& \qquad \gamma = \frac{\sqrt{2m\varepsilon}}{\hbar}$$

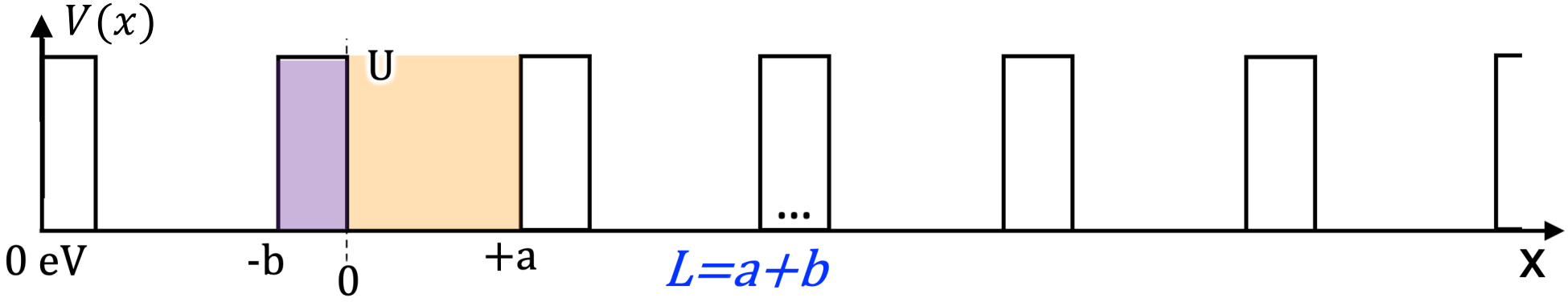
$$\cos(kL) = \underbrace{\left[\cos(\gamma a)\cosh(\beta b) + \frac{(\gamma^2+\beta^2)}{2\gamma\beta}\sin(\gamma a)\sinh(\beta b)\right]}_{W(\varepsilon)}$$

$$\therefore \cos(kR) = W(\varepsilon)$$

From Bloch theorem

$$\psi = \begin{cases} Ae^{+i\gamma x} + Be^{-i\gamma x}; 0<x<a \\ Ce^{+\beta x} + De^{-\beta x}; -b < x < 0 \end{cases}$$

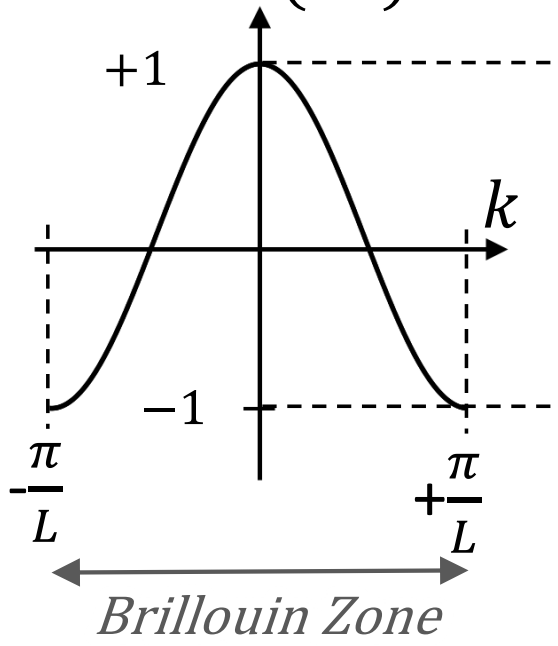
$$\psi(x+L) = e^{+ikL}\psi(x) \qquad V(x+L) = V(x)$$

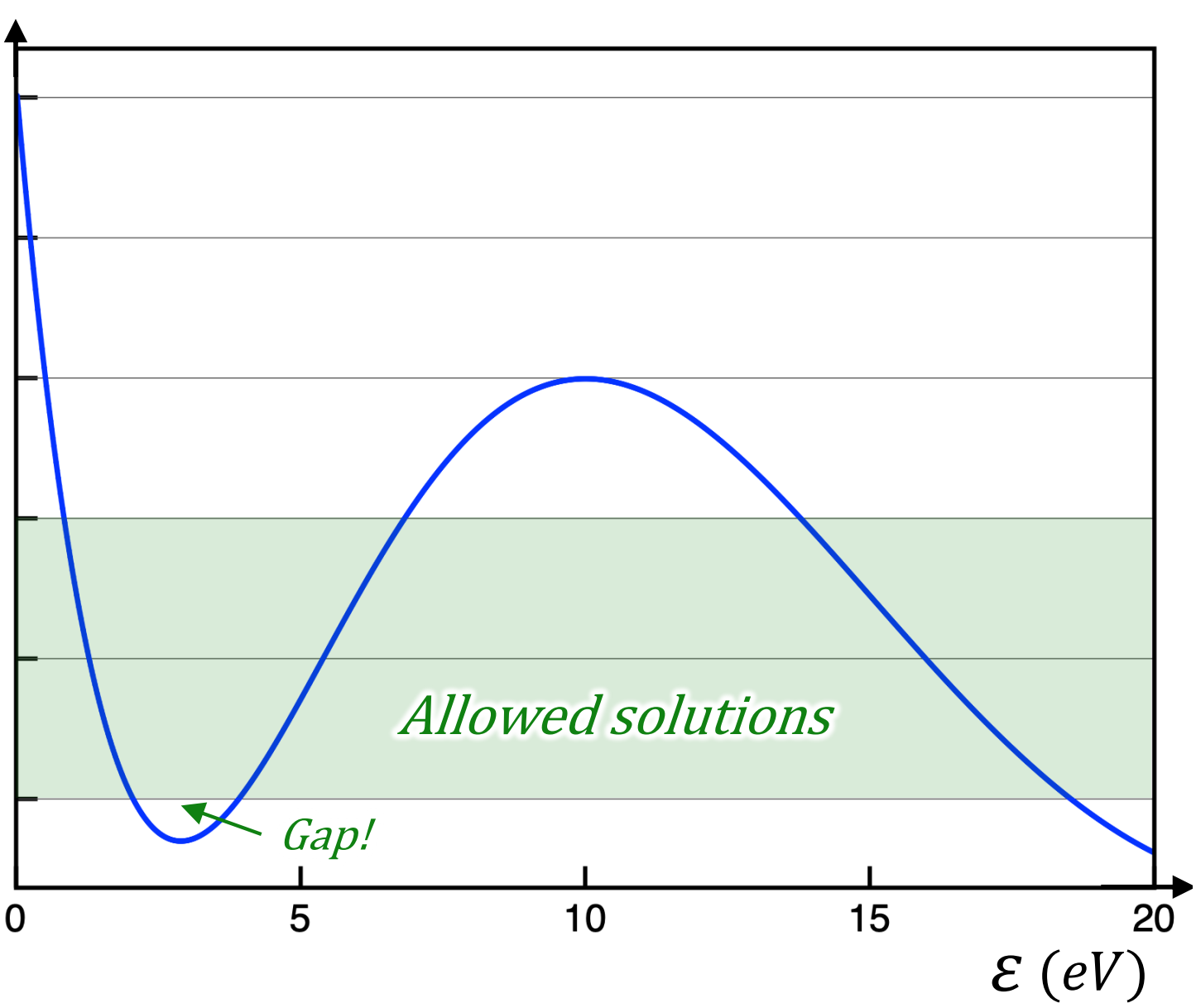


Crystals & Electrons : Quantum

=> Plot the equivalence... $\cos(kR) = W(\varepsilon)$

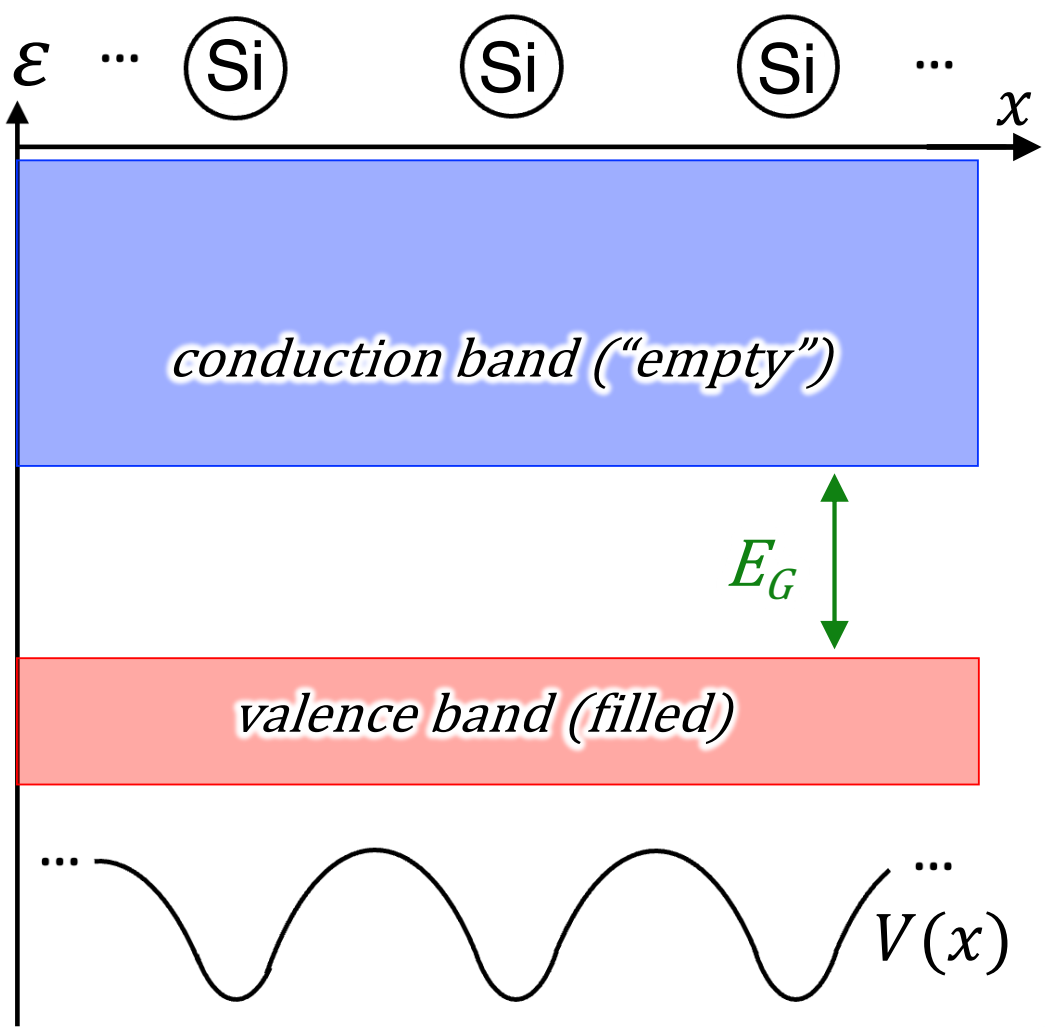
$L = |\boldsymbol{R}|$

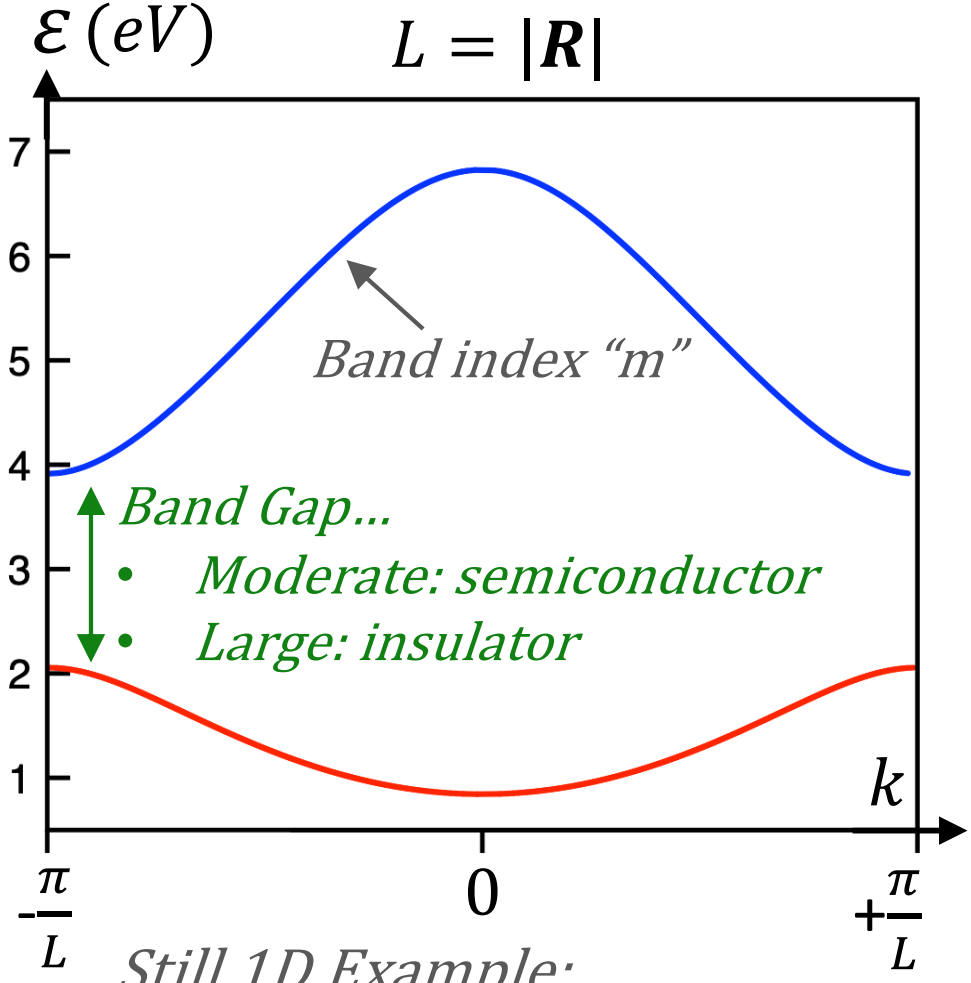




Crystals & Band Structure

=> Usually we plot allowed energies with respect to k....





Still 1D Example:

$$\varepsilon\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi$$

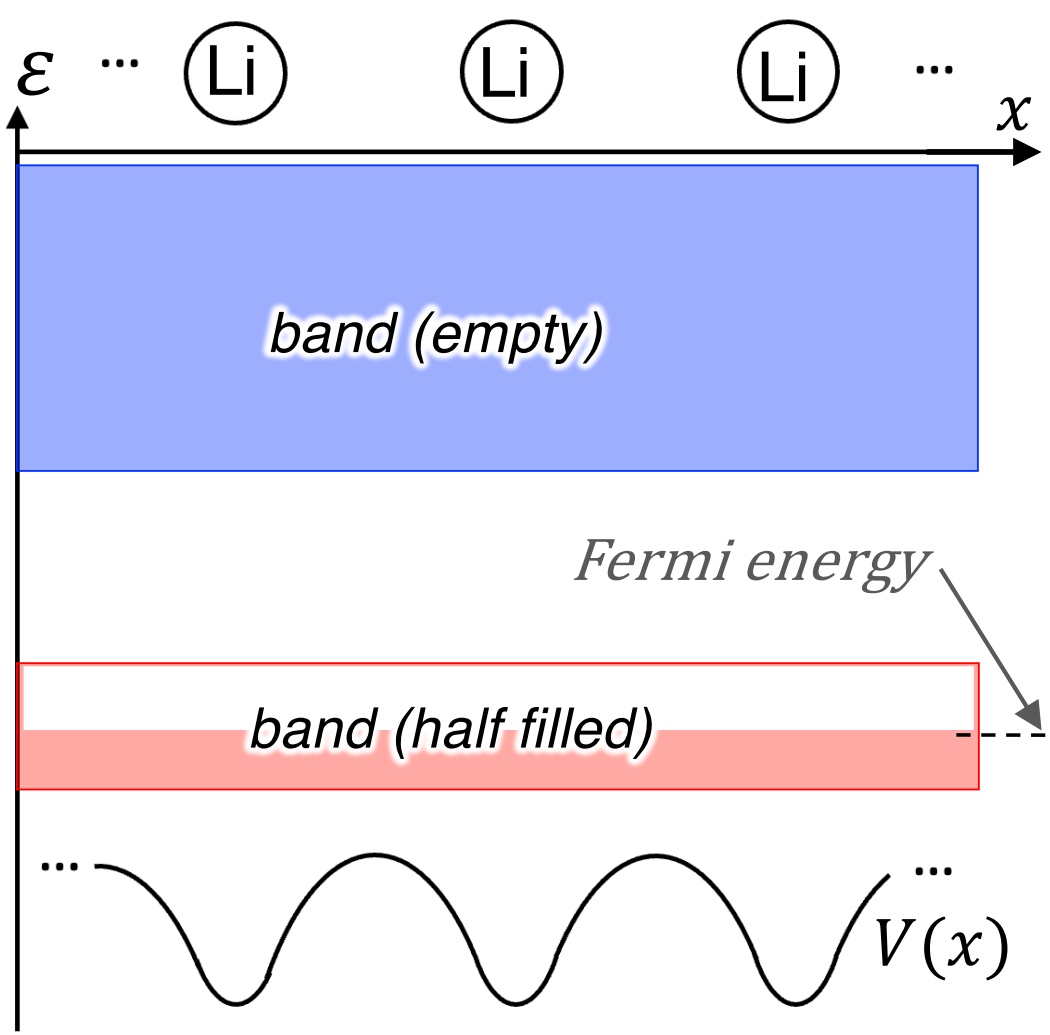
return indices

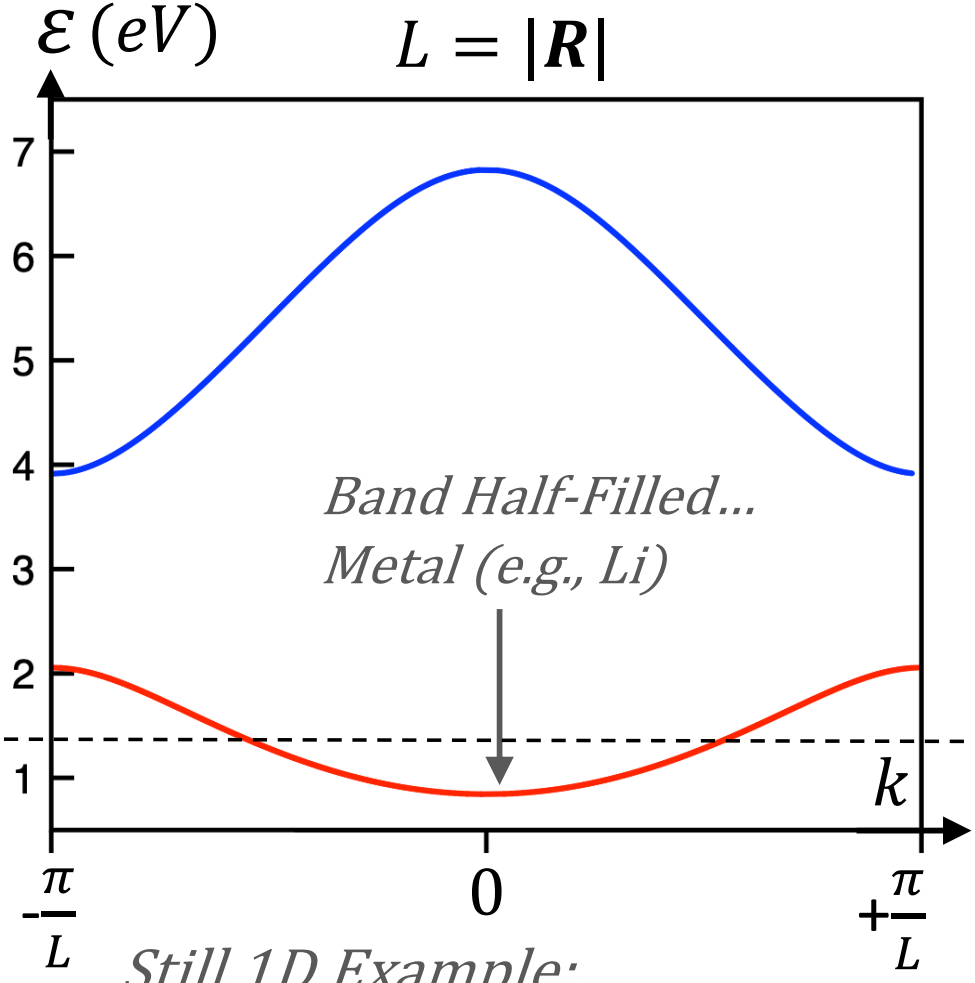
$$\psi_{m,k}(x) = e^{+i\boldsymbol{k}\cdot\boldsymbol{x}}\, u_{m,k}(x)$$

$$u_{m,k}(x+L) = u_{m,k}(x)$$

Crystals & Band Structure

=> Metals.... i.e., good conductors... (not necessarily elemental)...





Still 1D Example:

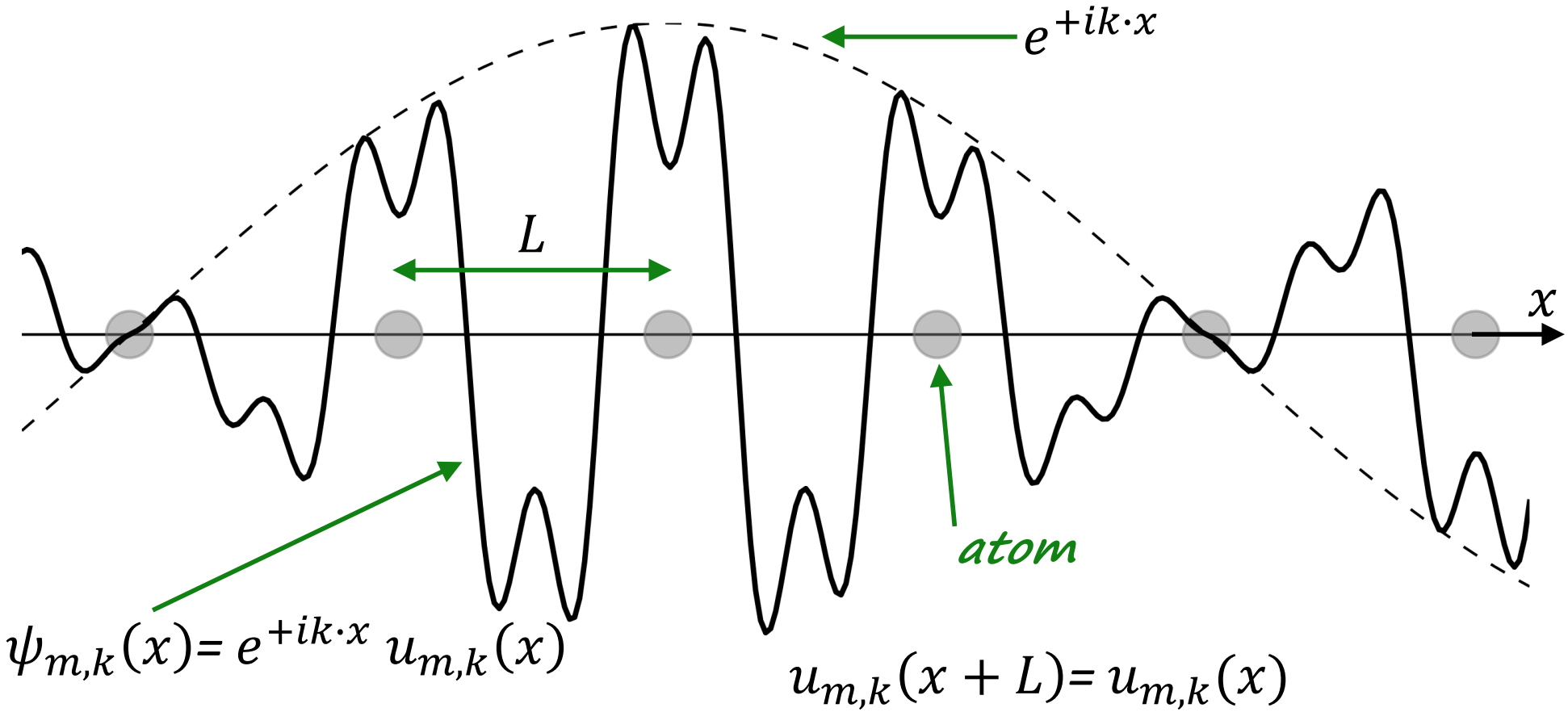
$$\psi_{m,k}(x) = e^{+i\mathbf{k}\cdot\mathbf{x}}\, u_{m,k}(x)$$

$$u_{m,k}(x+L) = u_{m,k}(x)$$

$$\varepsilon_{m,k}\psi_{m,k} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi_{m,k}$$

Crystals & Electron Waves

=> Why limit the Brillouin zone to $-\pi/L \rightarrow +\pi/L$? … Example…

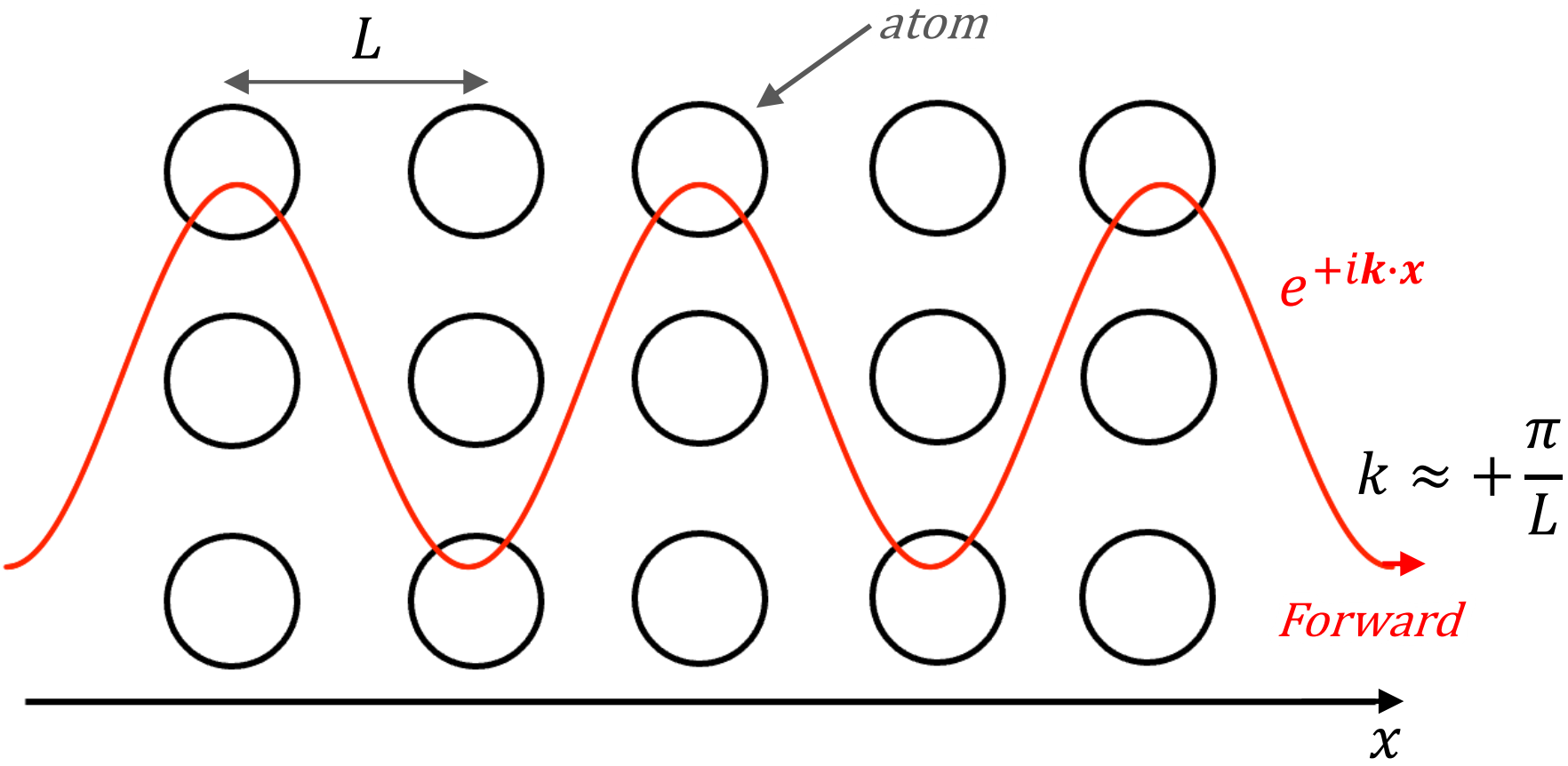


=> The envelope term ($e^{+ik\cdot x}$) cannot modulate the Bloch component ($u_{m,k}(x)$) with any periodicity less than π/L (2 unit cells) due to aliasing…

https://en.wikipedia.org/wiki/Bloch's_theorem

Crystals & Electron Waves

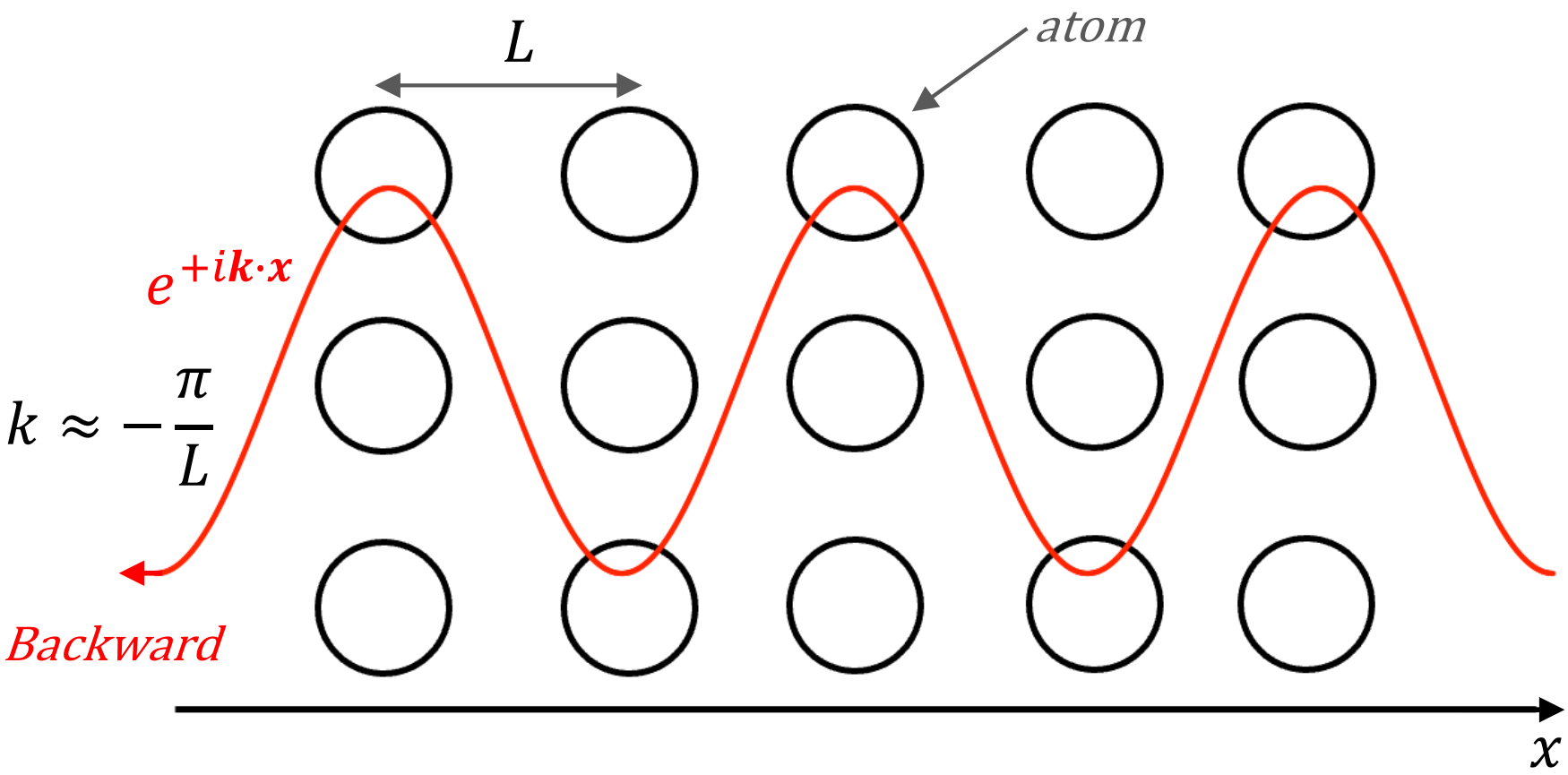
=> Why limit the Brillouin zone to $-\pi/L \rightarrow +\pi/L$? ... Example...



=> Moreover, $-\pi/L<k<0$ represents backwards travelling (electron) waves on the lattice and $0<k<+\pi/L$ forwards waves...

Crystals & Electron Waves

=> Why limit the Brillouin zone to -π/L -> +π/L ? ... Example...



=> Moreover, -π/L<k<0 represents backwards travelling (electron) waves on the lattice and 0<k<+π/L forwards waves...

Crystals & Electron Waves

=> Electron waves exist in a similar manner in all crystals (periodic arrangements of atoms).... extension to 3D...

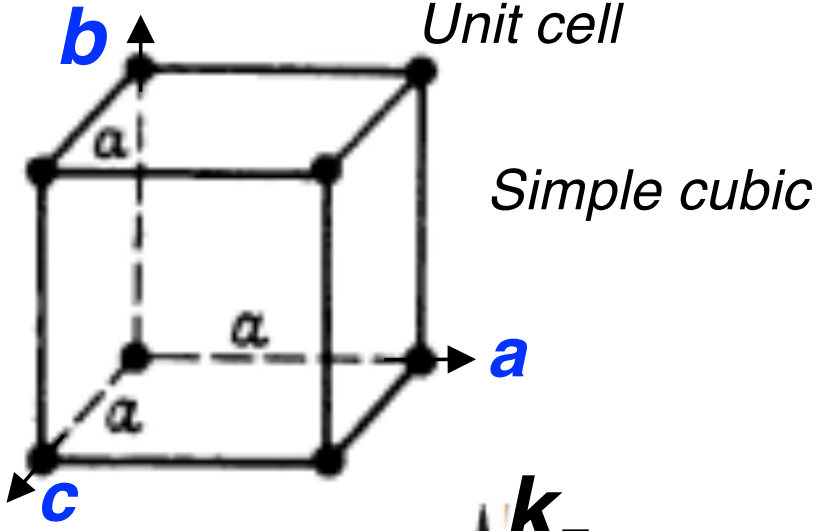
Reciprocal vectors:

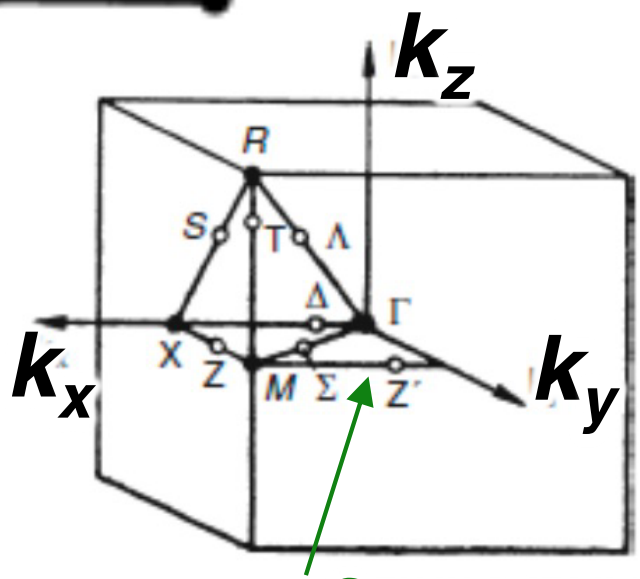
$$\mathbf{G}_x = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}$$

$$\mathbf{G}_y = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})}$$

$$\mathbf{G}_z = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})}$$

$$-\mathbf{G}_j/2 < \mathbf{k}_j \leq \mathbf{G}_j/2 \qquad j \in (x,y,z)$$



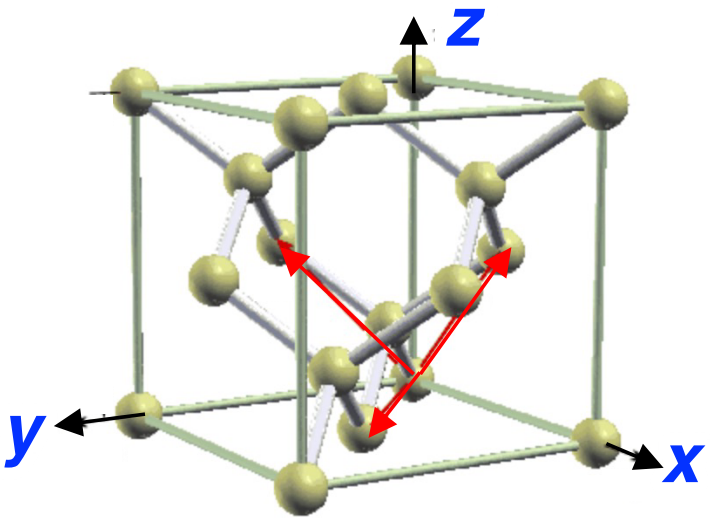


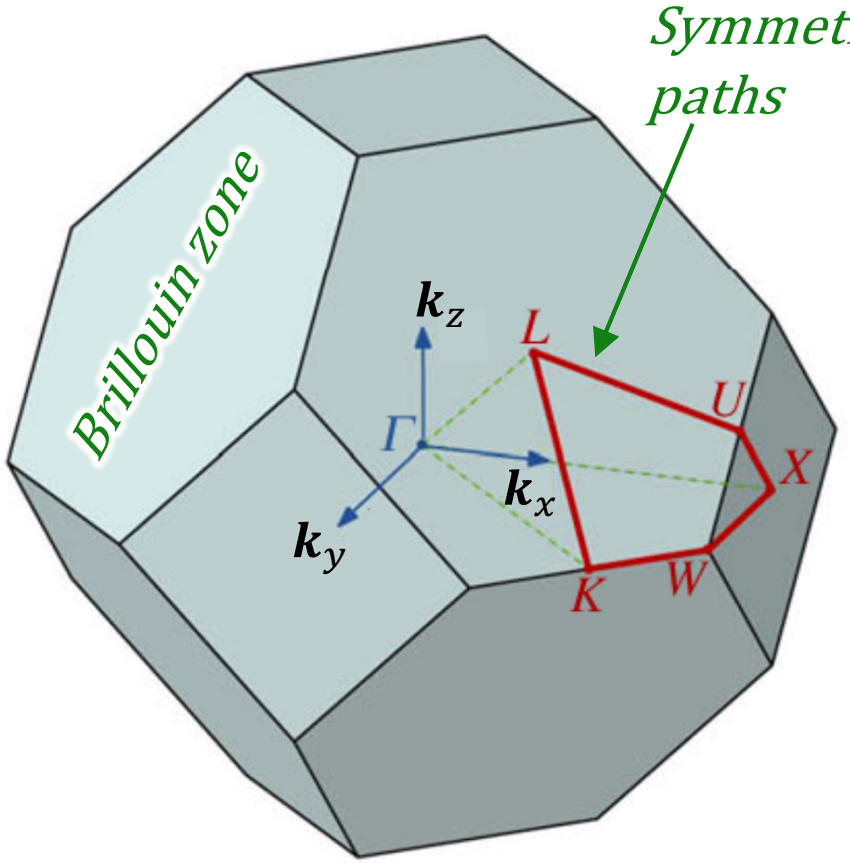
Symmetry paths in Brillouin zone

=> Similar reciprocal vectors exist for all unit cells and their electrons.

Crystals & Electron Waves

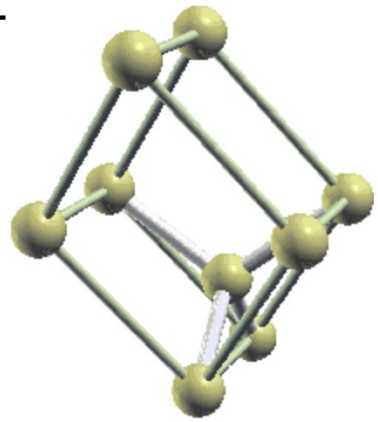
=> More "exotic" Brillion zones for more complex unit cells, e.g. diamond lattice (silicon) …





DOI:10.1098/rsif.2011.0730

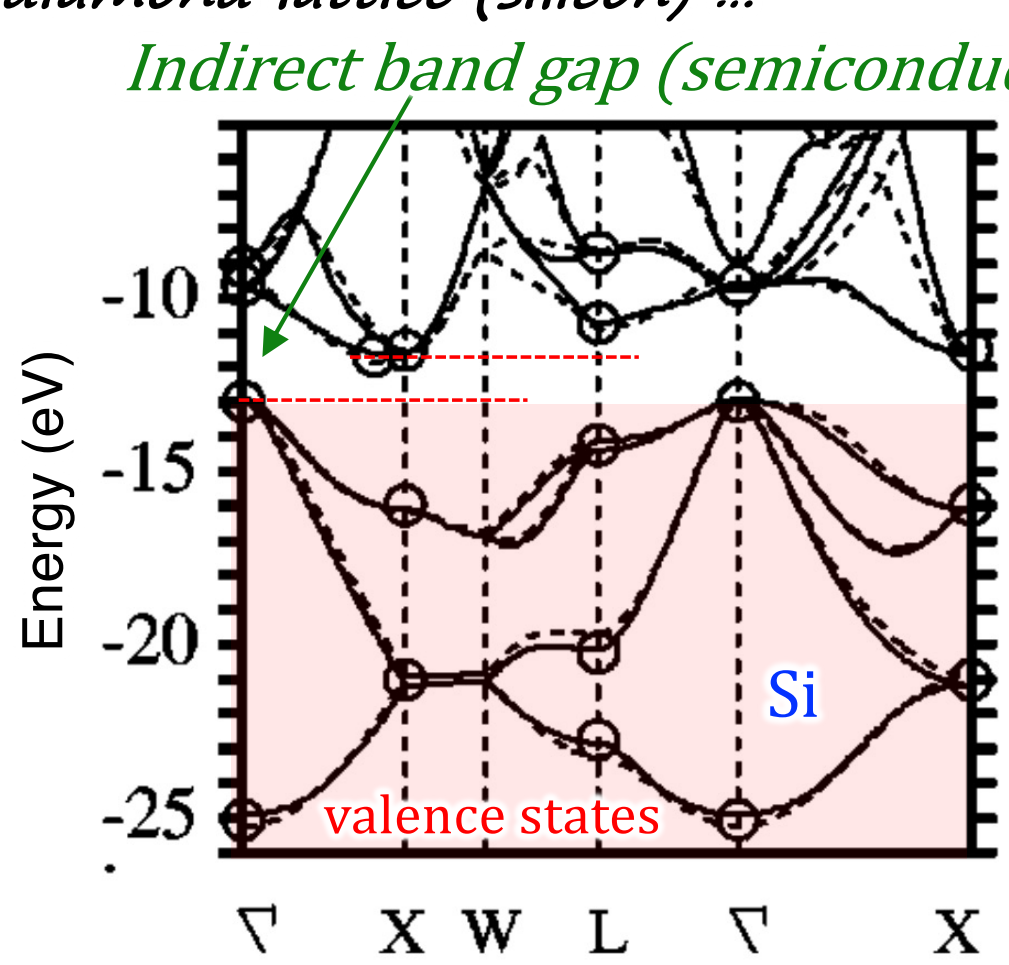
primitive diamond unit cell (important for electronic properties)



Classic Text: "Symmetry and energy bands in crystals", J. C. Slater (1972).

Crystals & Electronic Properties

=> More "exotic" Brillion zones for more complex unit cells, e.g. diamond lattice (silicon) …



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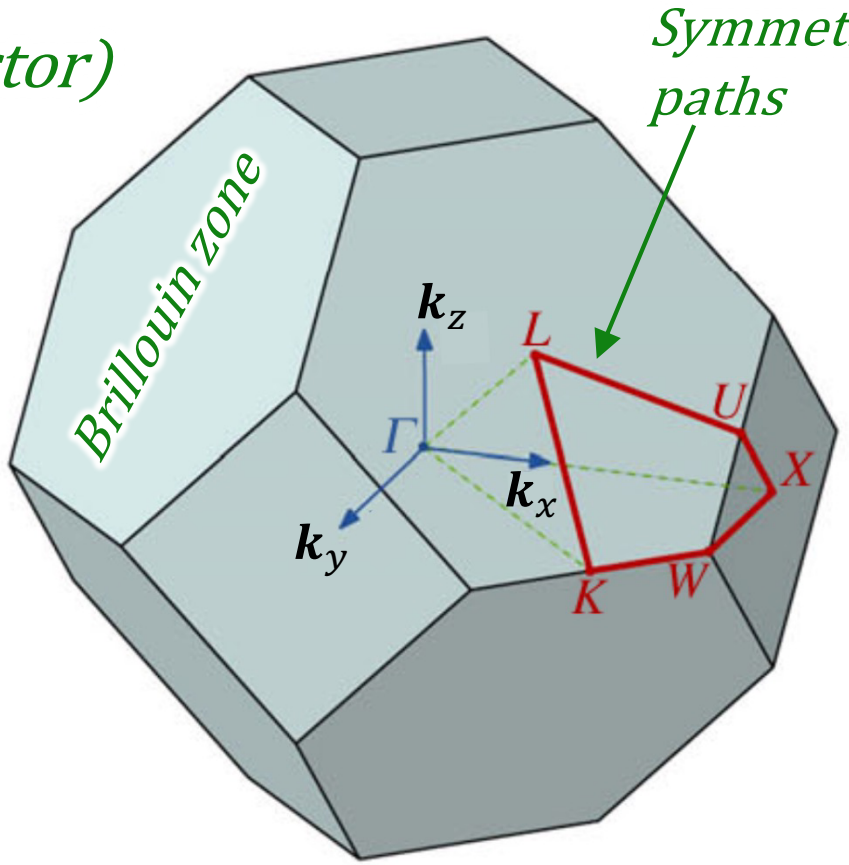


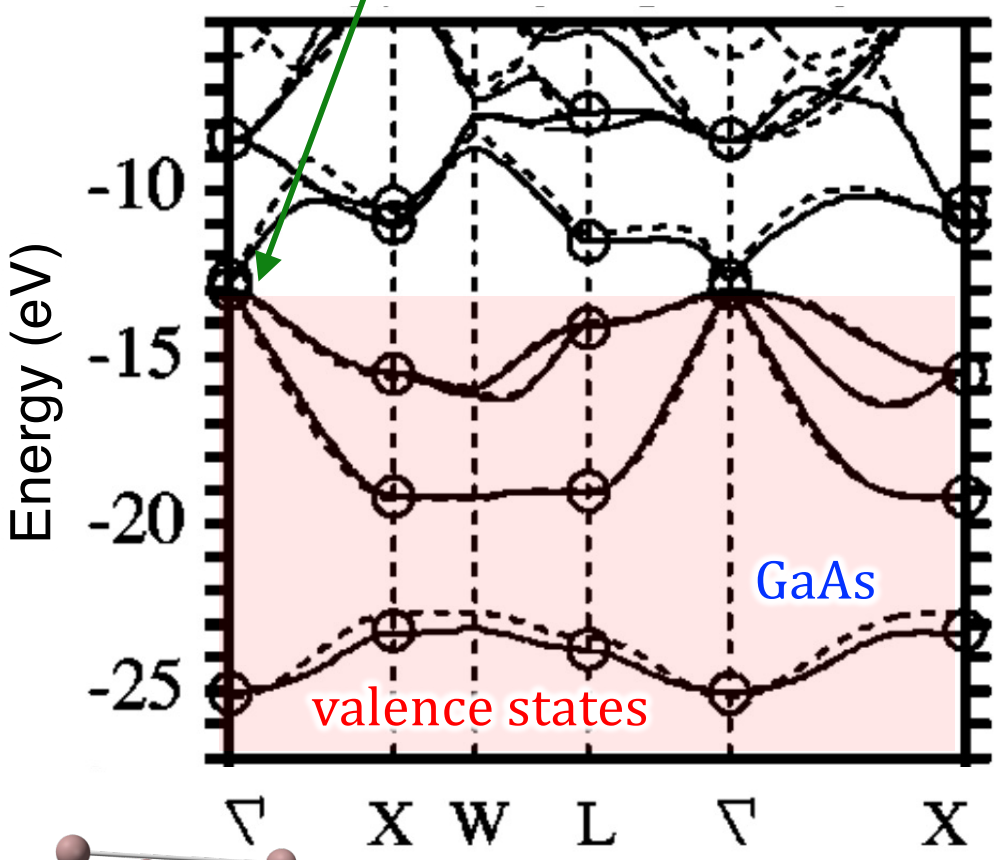
DOI:10.1098/rsif.2011.0730

=> Band structure plots trace these symmetry paths and can reveal important materials insights…

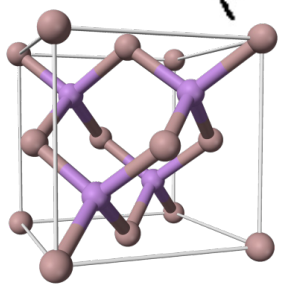
Crystals & Electronic Properties

=> Direct band gap materials absorb light more efficiently...

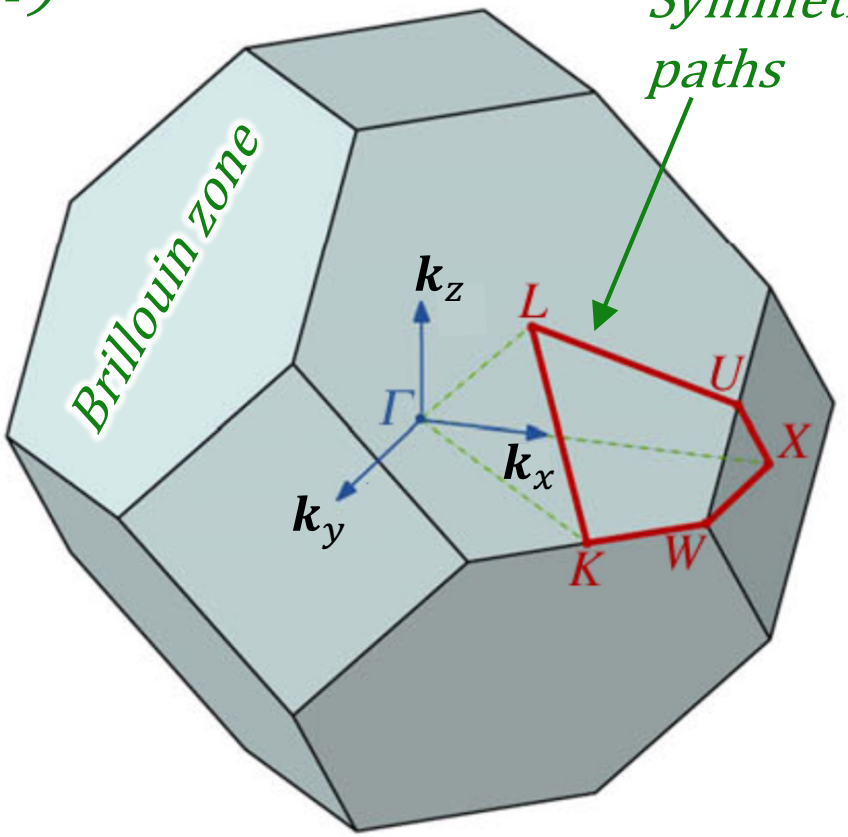
Direct band gap (semiconductor)



Phys. Rev. B **61**, 7965 (2000)



Symmetry paths



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...band structure unique to each material...

Crystals & Electron Waves

=> Takeaways….

- Periodicity in the lattice gives rise to periodicity in the electron density;
- Electrons ”move” as waves on crystal lattices;
- The energies of various electron wavevectors, band structure, gives important electronic structure (metal, semiconductor, insulator) and optical information.

=> Missing….

- How to solve systems when there is periodicity in the electron density?
- How does periodicity in the electron density (& lattice) impact on the Hamiltonian and solution procedures?
- Anything more to the “ion-core” approximation?

Hartree units

$$\varepsilon_{m,k}\psi_{m,k} = \left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r})\right]\psi_{m,k}$$

$$\vdots$$

….pardon typos/errors within.