Density-Functional Theory for Practitioners - Lecture 3

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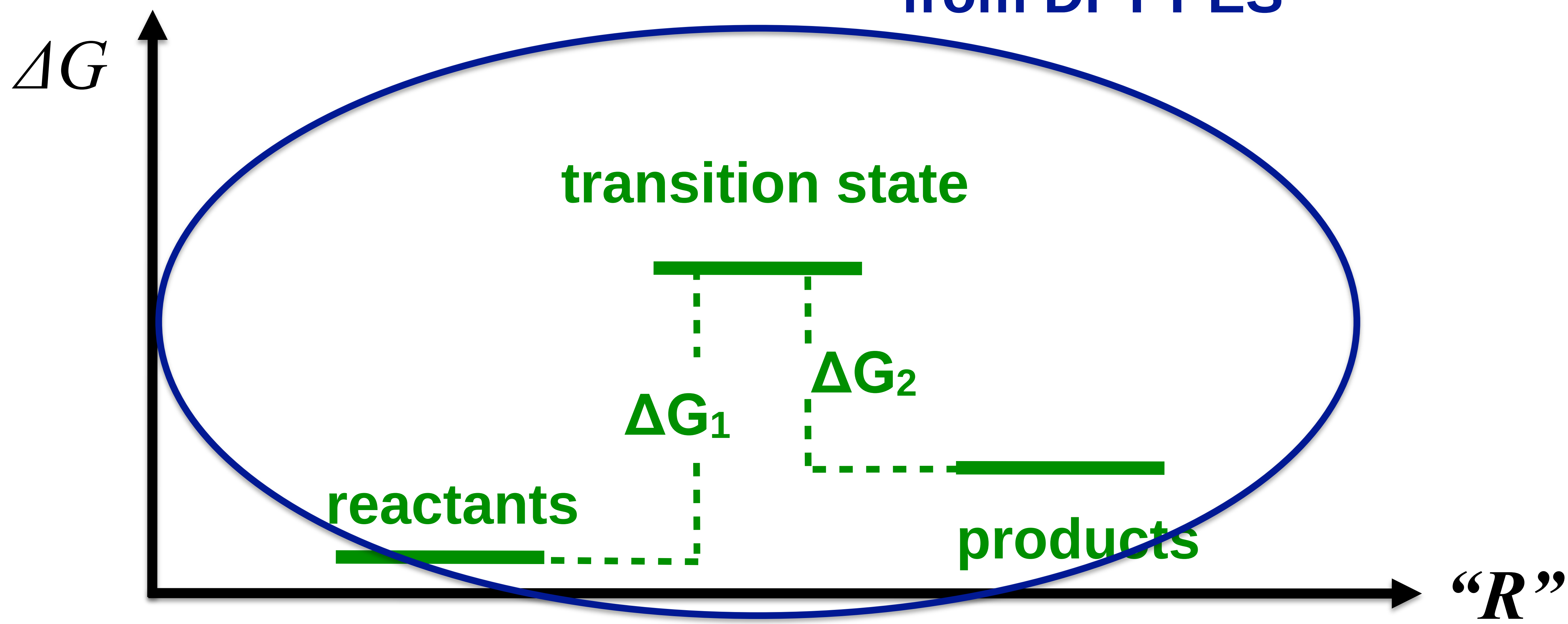
Revision

At your table, reflect on last week's lecture and tutorial:

- What did you learn about the equilibrium structure of molecules?
- What did you find difficult or easy in running the calculations?
- How did the calculations help you understand DFT better?

House keeping – Chemical reactions

from DFT PES



$$\Delta G = \Delta H - T\Delta S$$
$$\approx \Delta H$$
$$\approx \Delta E + p\Delta V$$

DFT

Important unless ΔE ~ 0.2 eV ~ 20kJ/mol

House keeping – geometry.in > initial_moment

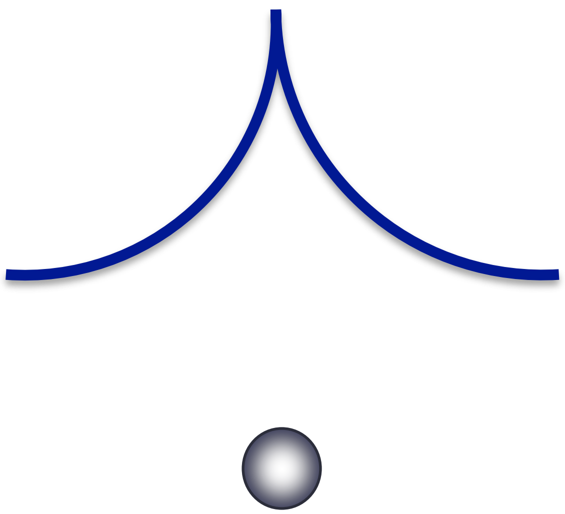
Electron Configurations of Selected Elements

Element	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s	Electron configuration
H	↑						$1s^1$
He	↑↓						$1s^2$
Li	↑↓	↑					$1s^2 2s^1$
C	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑		$1s^2 2s^2 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p^6$
Na	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

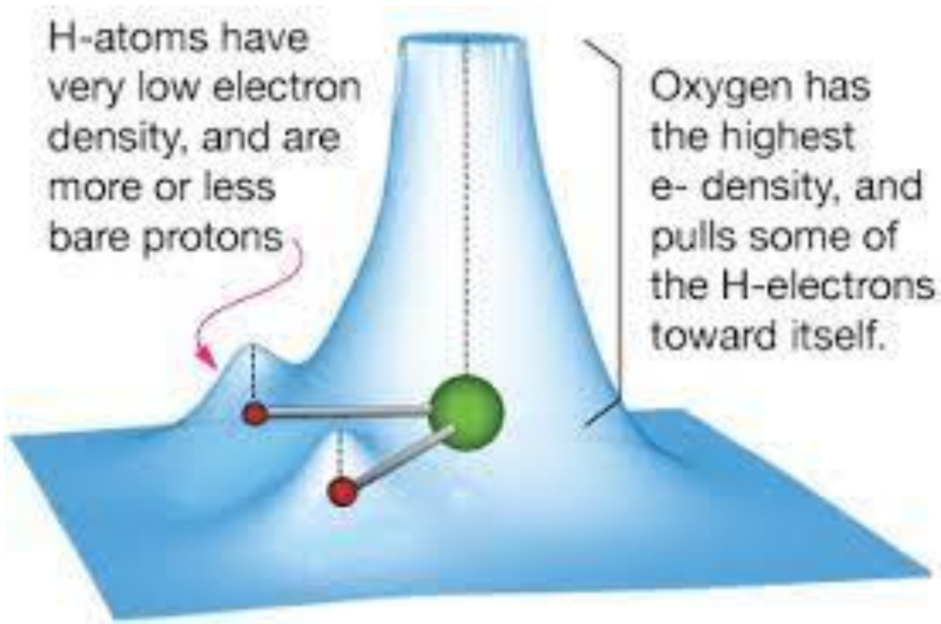
initial_moment 1
initial_moment 0
initial_moment 1
initial_moment 2
initial_moment 3
initial_moment 2
initial_moment 1
initial_moment 0
initial_moment 1

House keeping – real-space density plotting

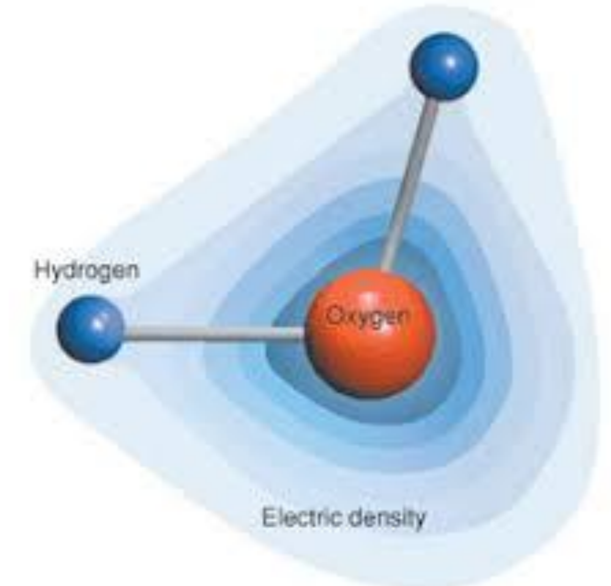
1D (line) -> 1D projection

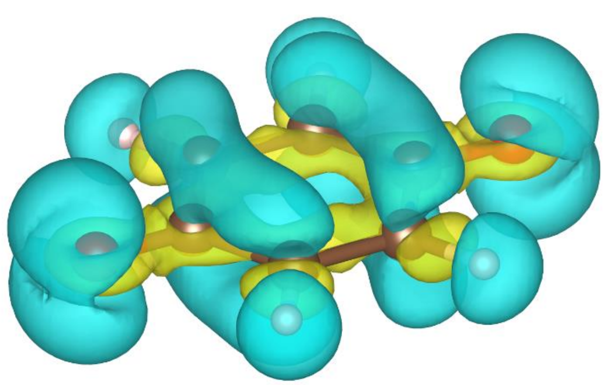


2D (plane) -> 1D projection



3D -> 1D projection - isosurfaces





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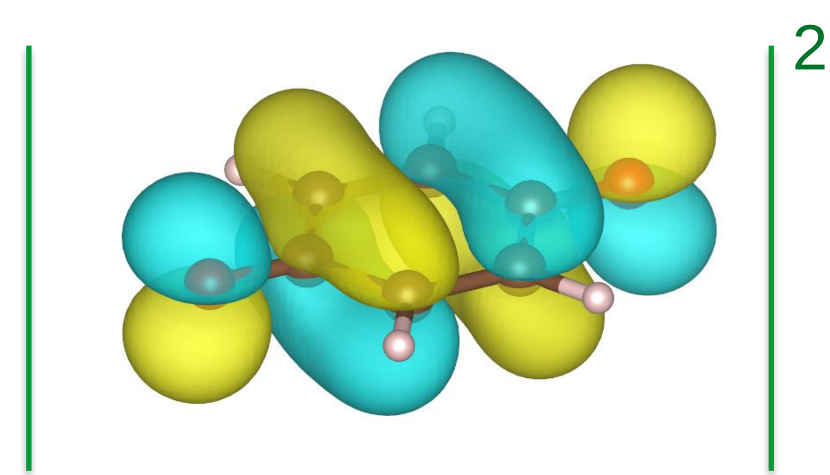


This lesson

Must know	Should know	Nice to know
Principles of bonding	Different bonding types	Bond formation
Periodic boundary conditions	Reciprocal space	Brillouin zone
Unit cell	Band structure	Distinction between metals, semiconductors, insulators

Learning outcomes

After completion of this class you

- are familiar with bonding and how it manifests in the charge density.
- know periodic boundary conditions and reciprocal space.
- can discriminate different solids.

Observations from Tutorial 2

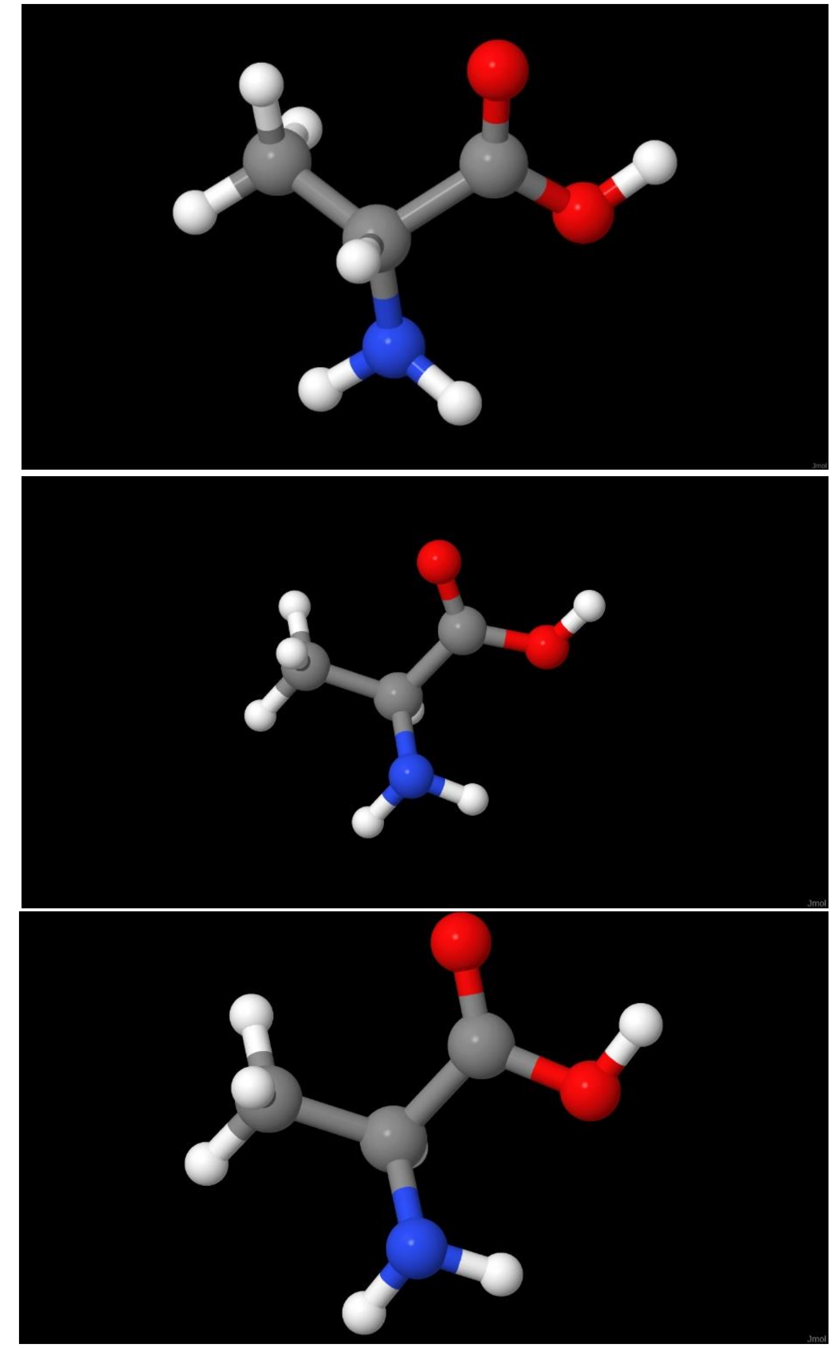
-8794.48 eV (charge +1) →

-8803.34 eV

-8794.74 eV (charge +1) ↘

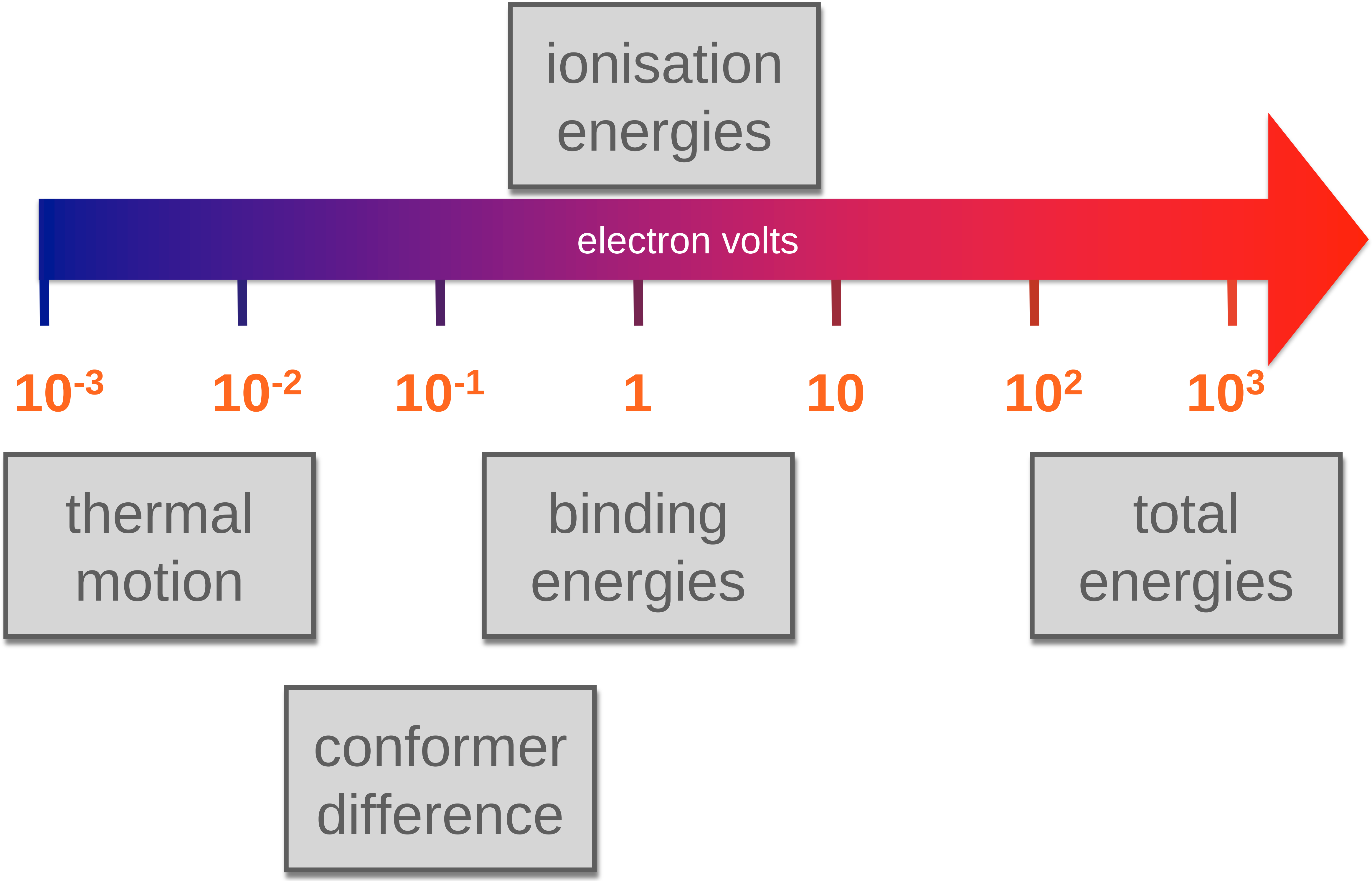
-8803.90 eV (tier 3)↘

-8803.38 eV

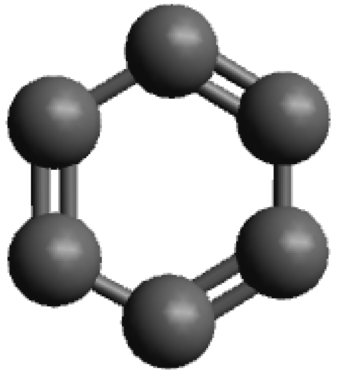


- **Total energies are large.**
- **Difference between conformers only ~0.1 eV.**
- **But, at room temperature:**
  $k_B T$=0.025 eV
- **Ionization energy ~10 eV.**

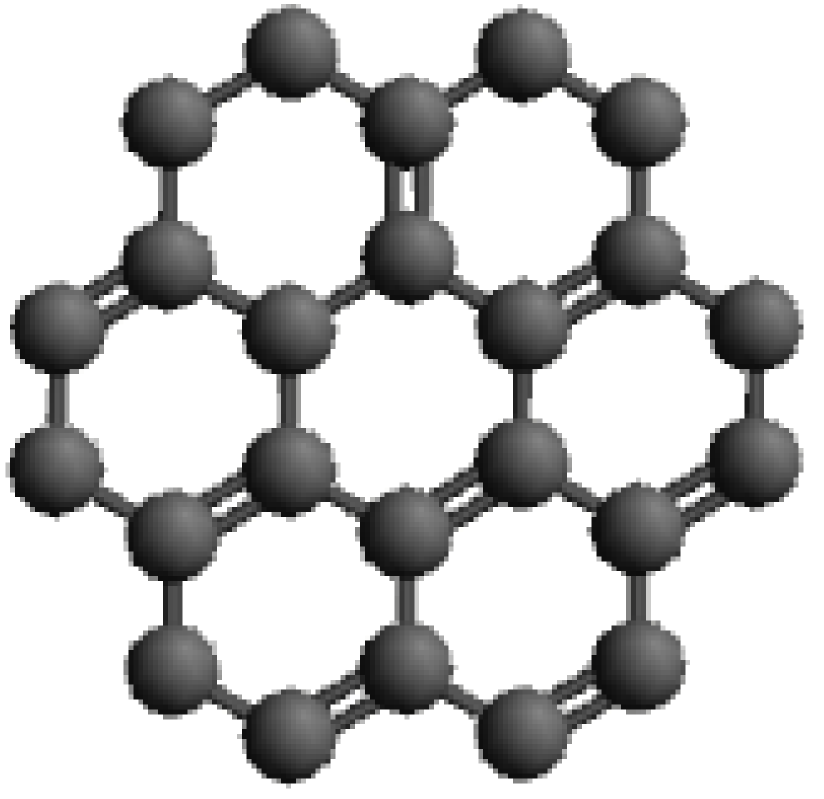
Energy scale



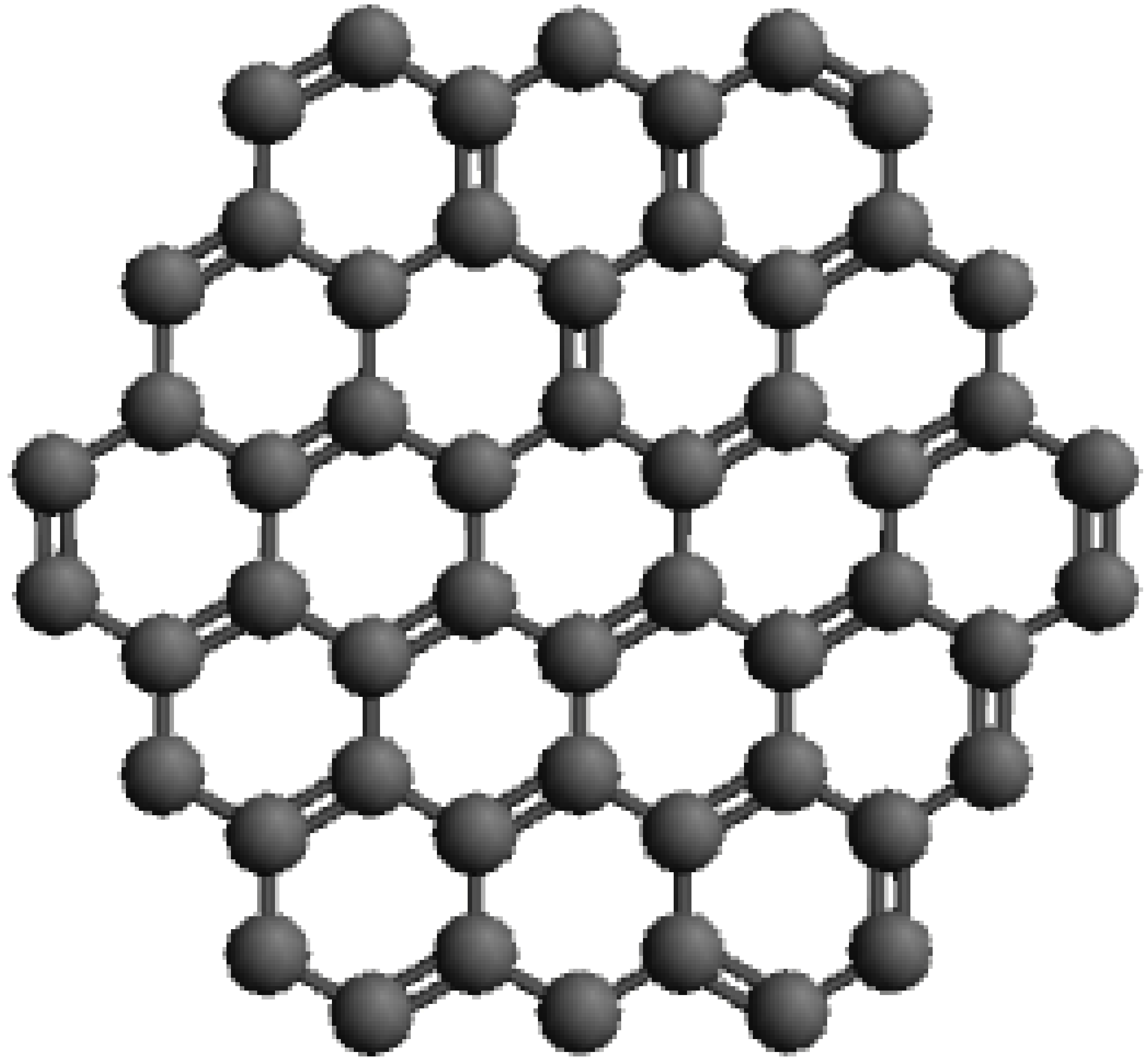
Periodic systems



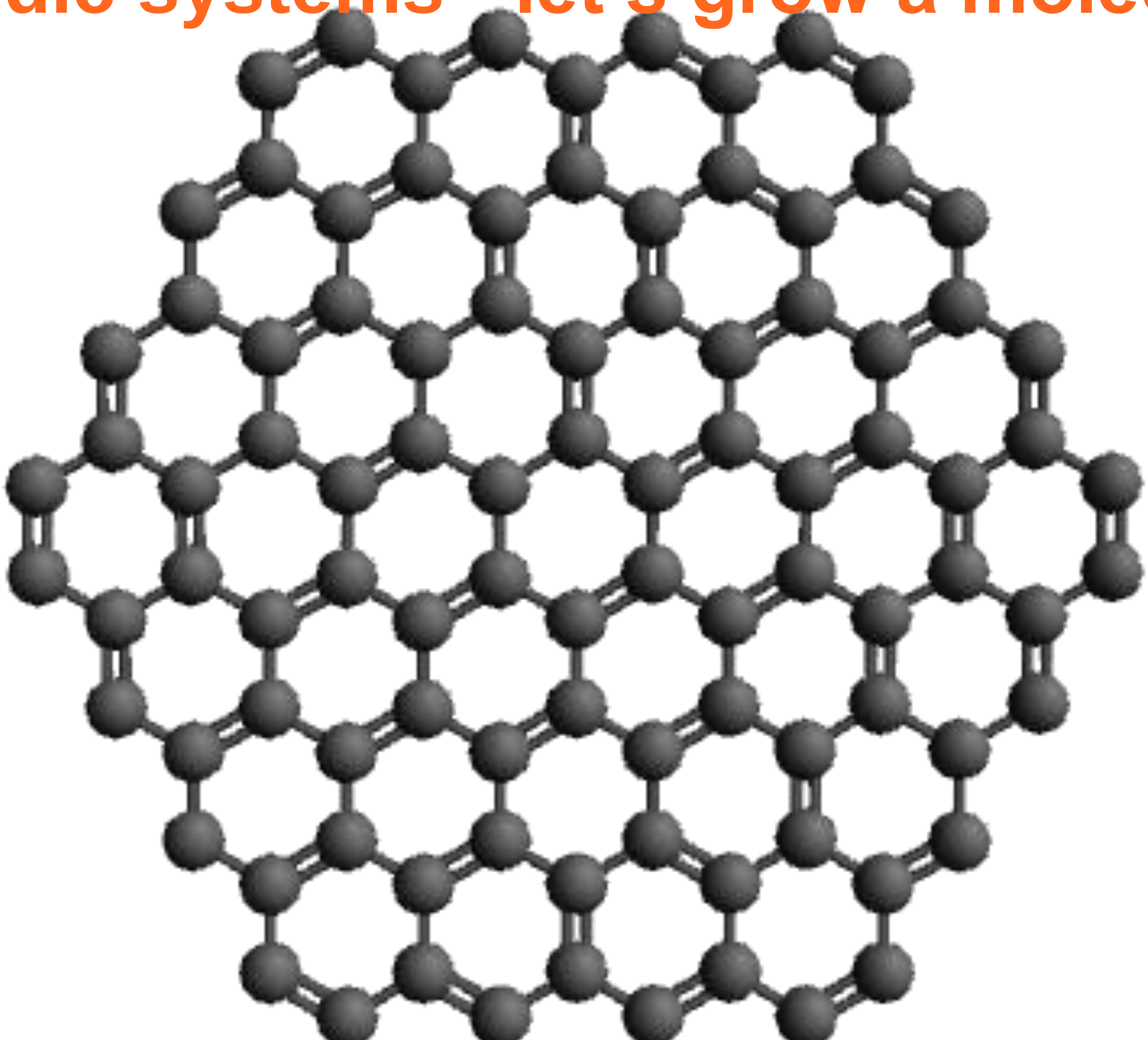
Periodic systems - let’s grow a molecule



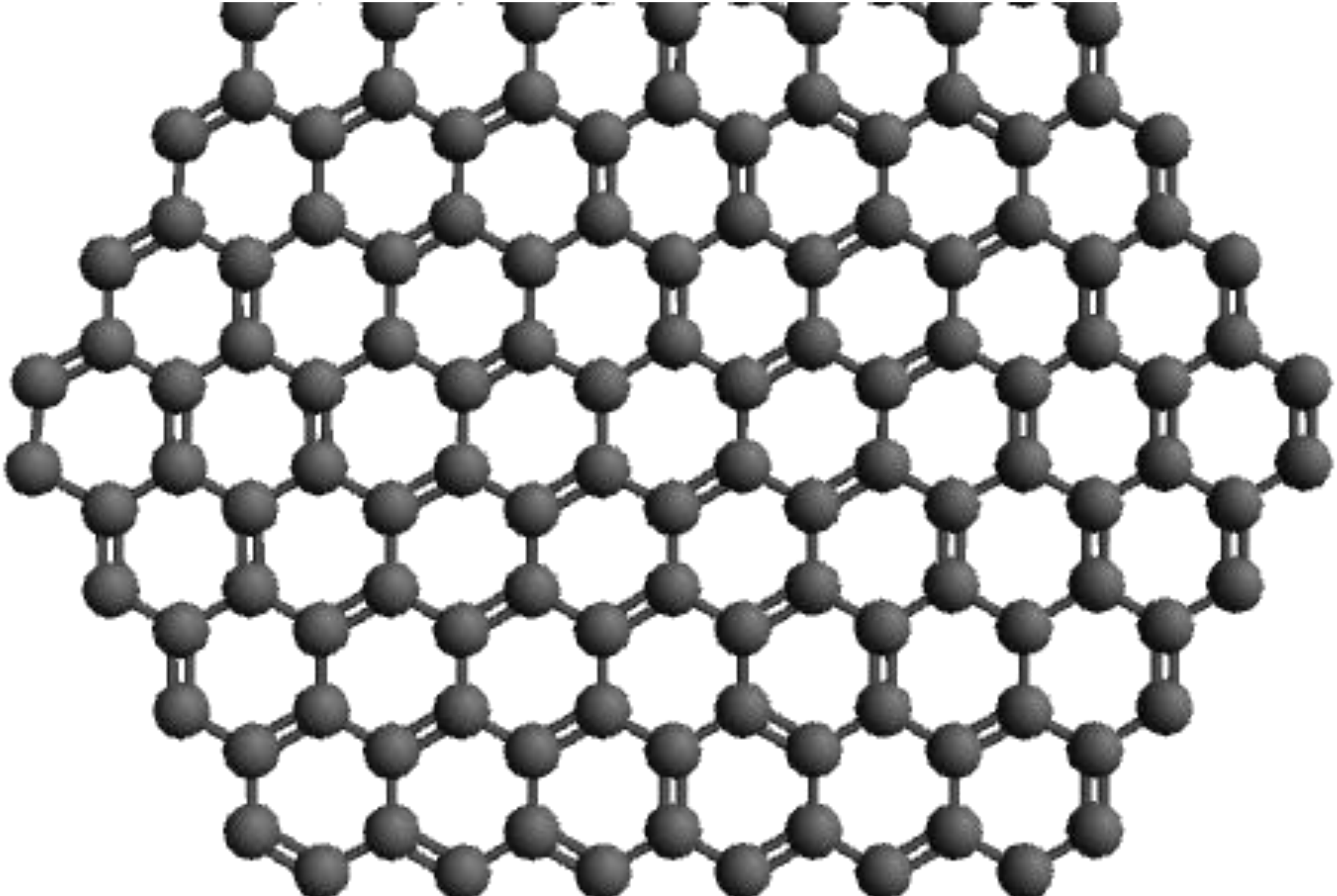
Periodic systems - let's grow a molecule



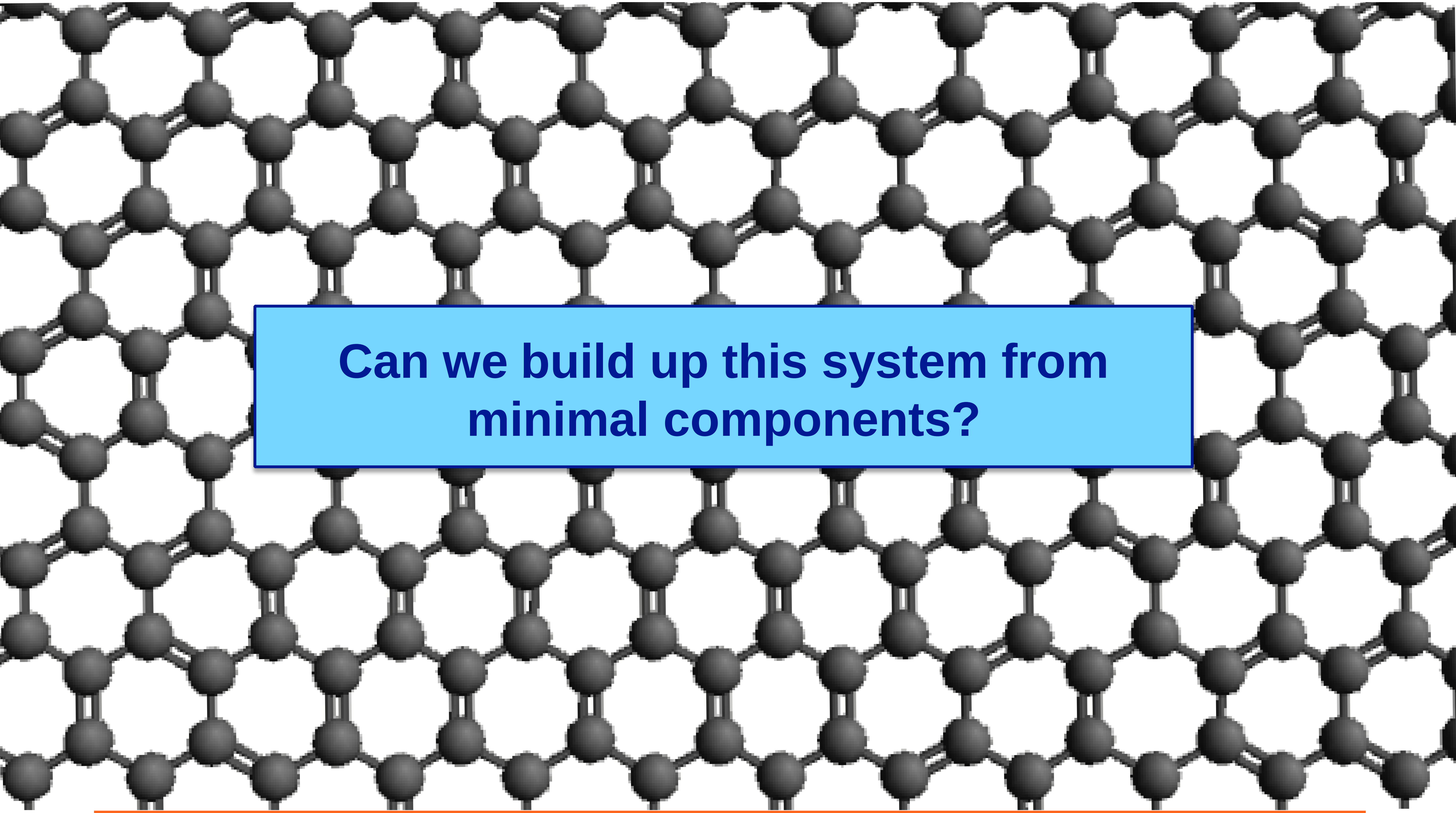
Periodic systems - let’s grow a molecule



Periodic systems - let's grow a molecule

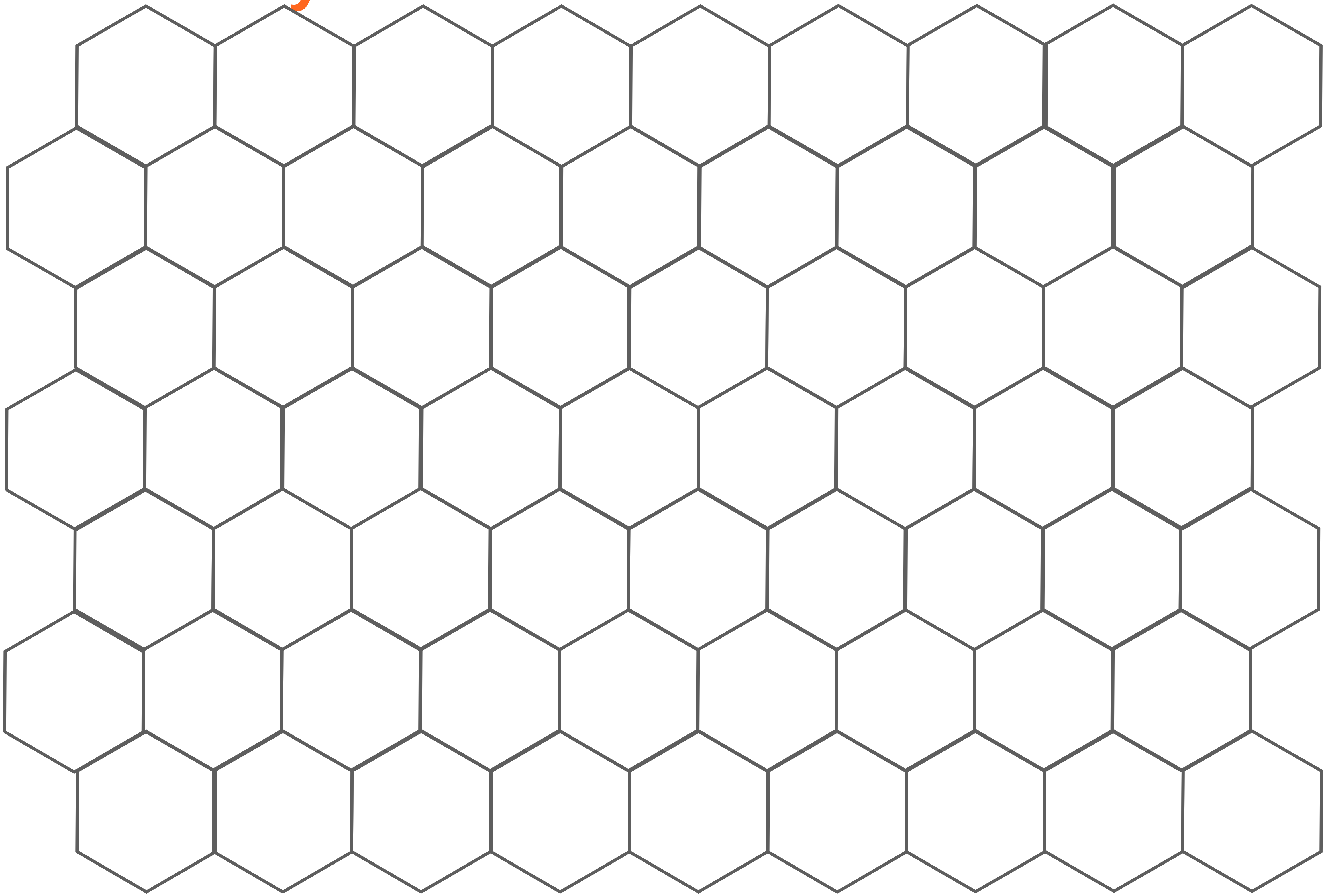


Periodic system

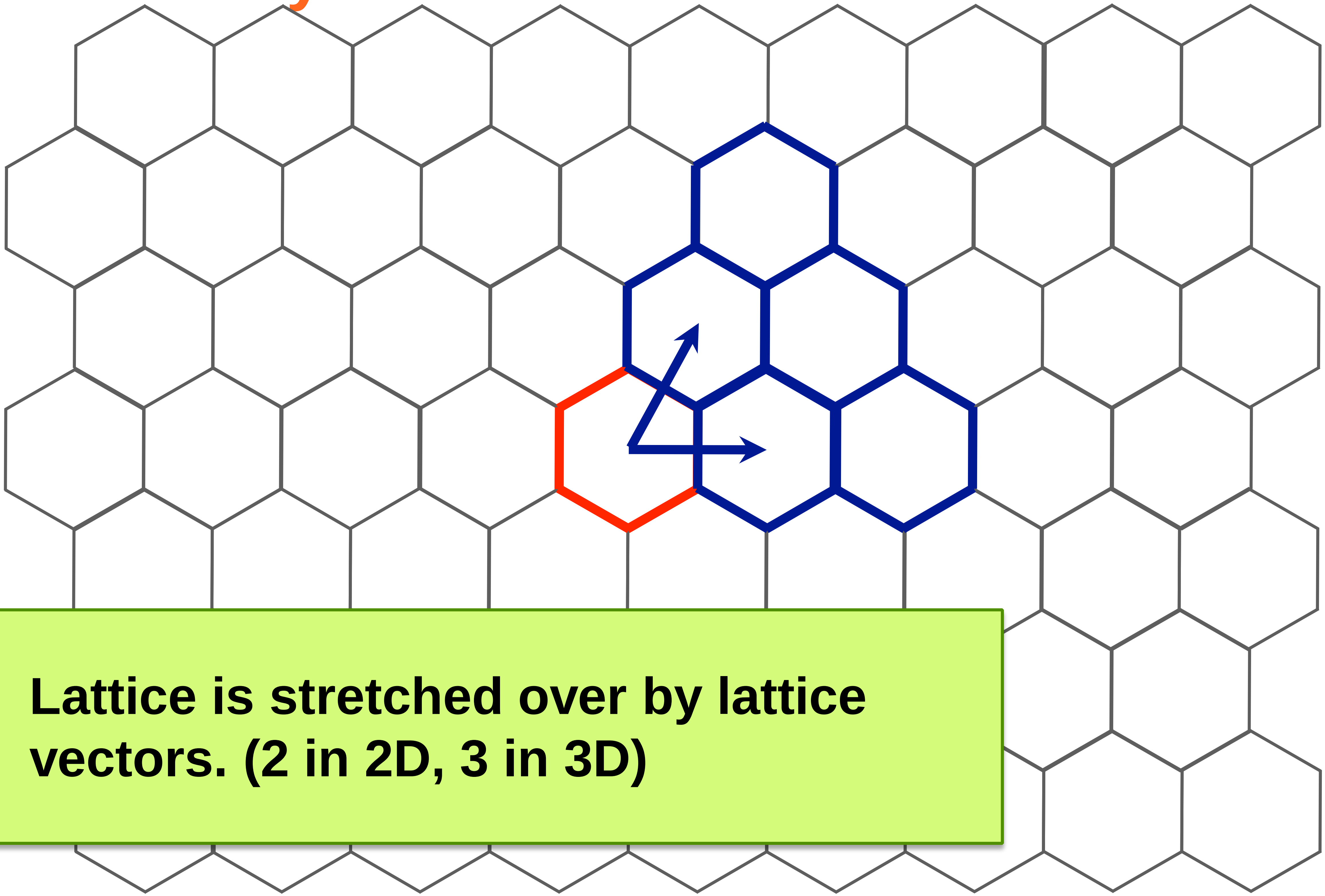


Can we build up this system from minimal components?

Periodic systems — lattice



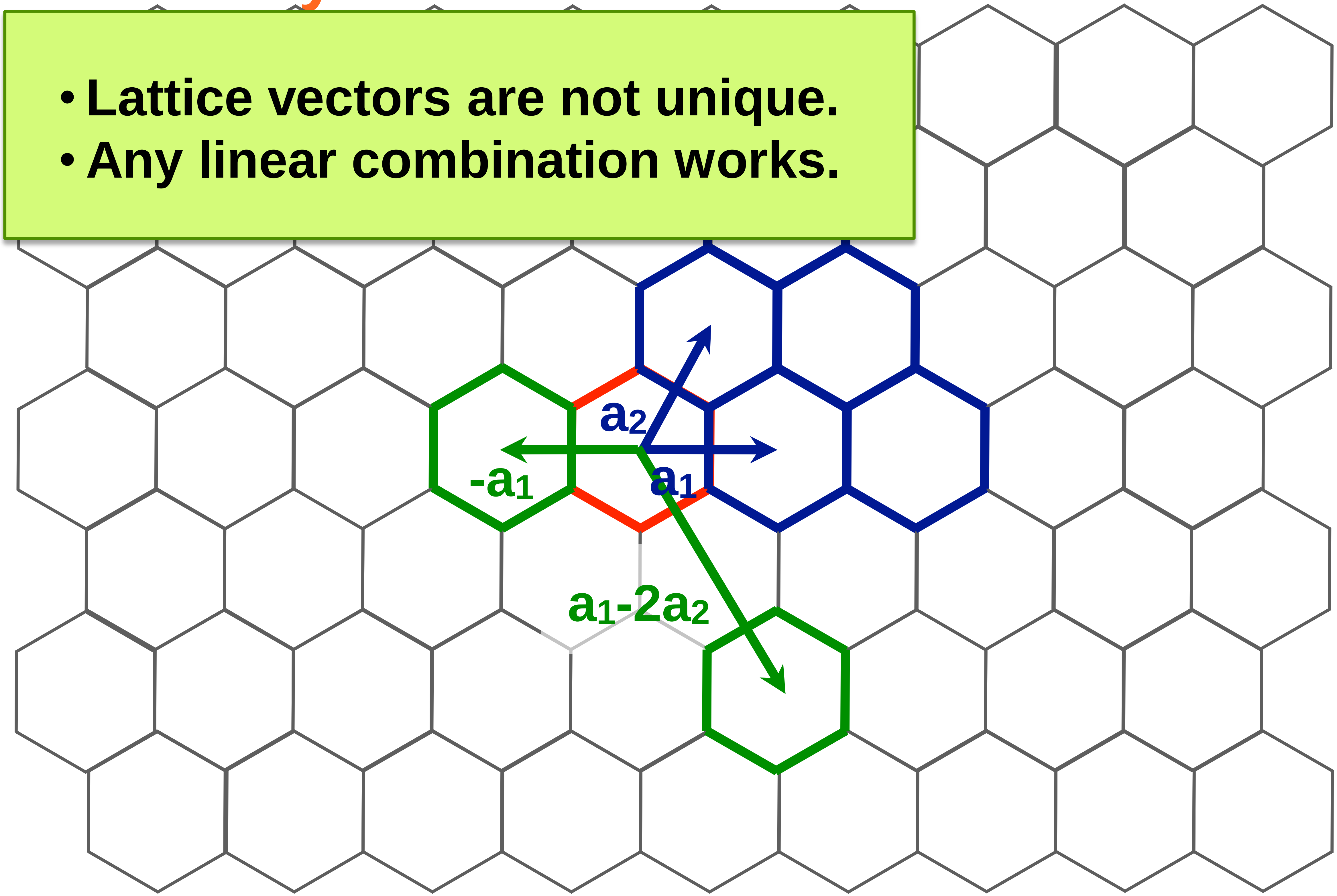
Periodic systems — lattice



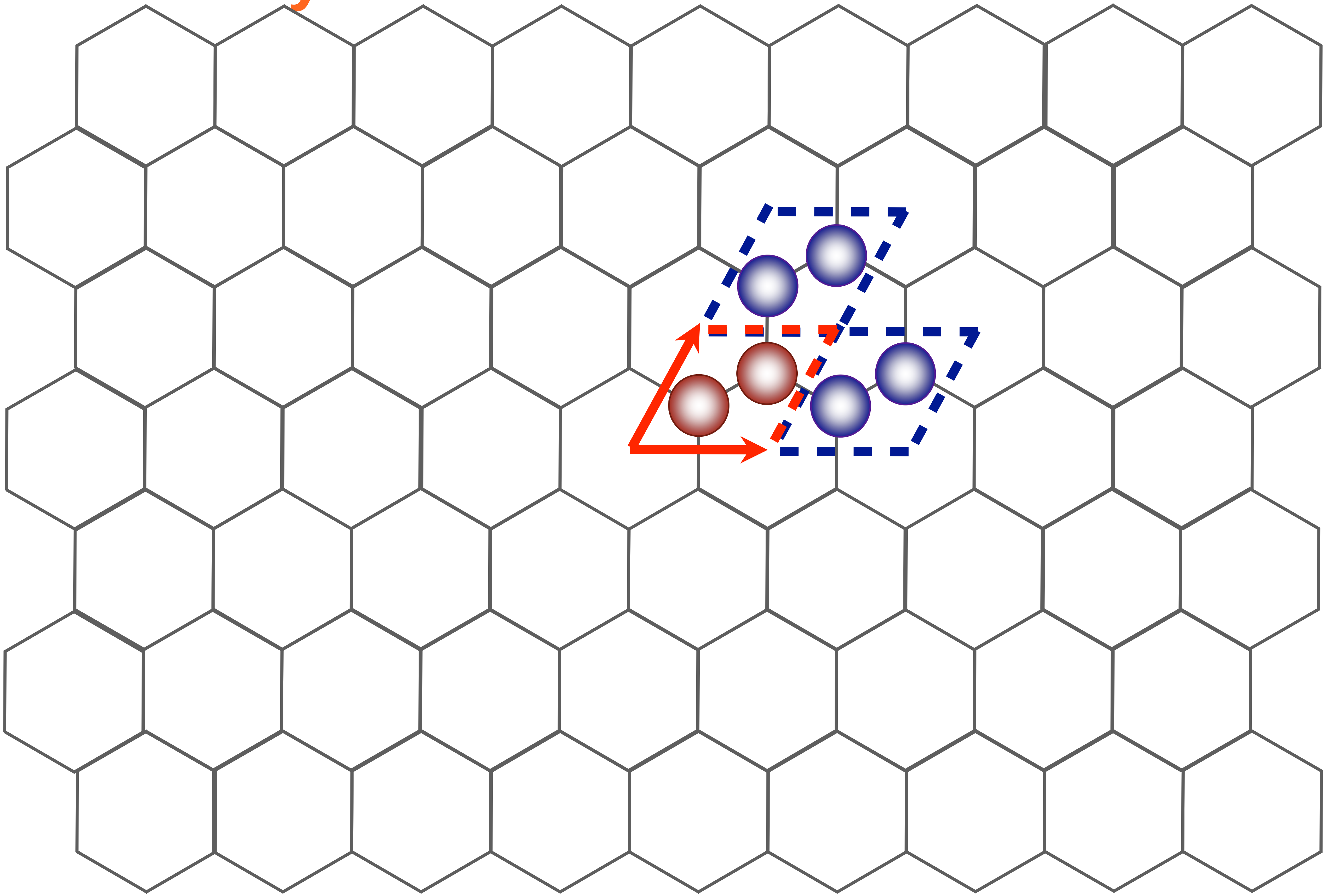
Lattice is stretched over by lattice vectors. (2 in 2D, 3 in 3D)

Periodic systems — lattice

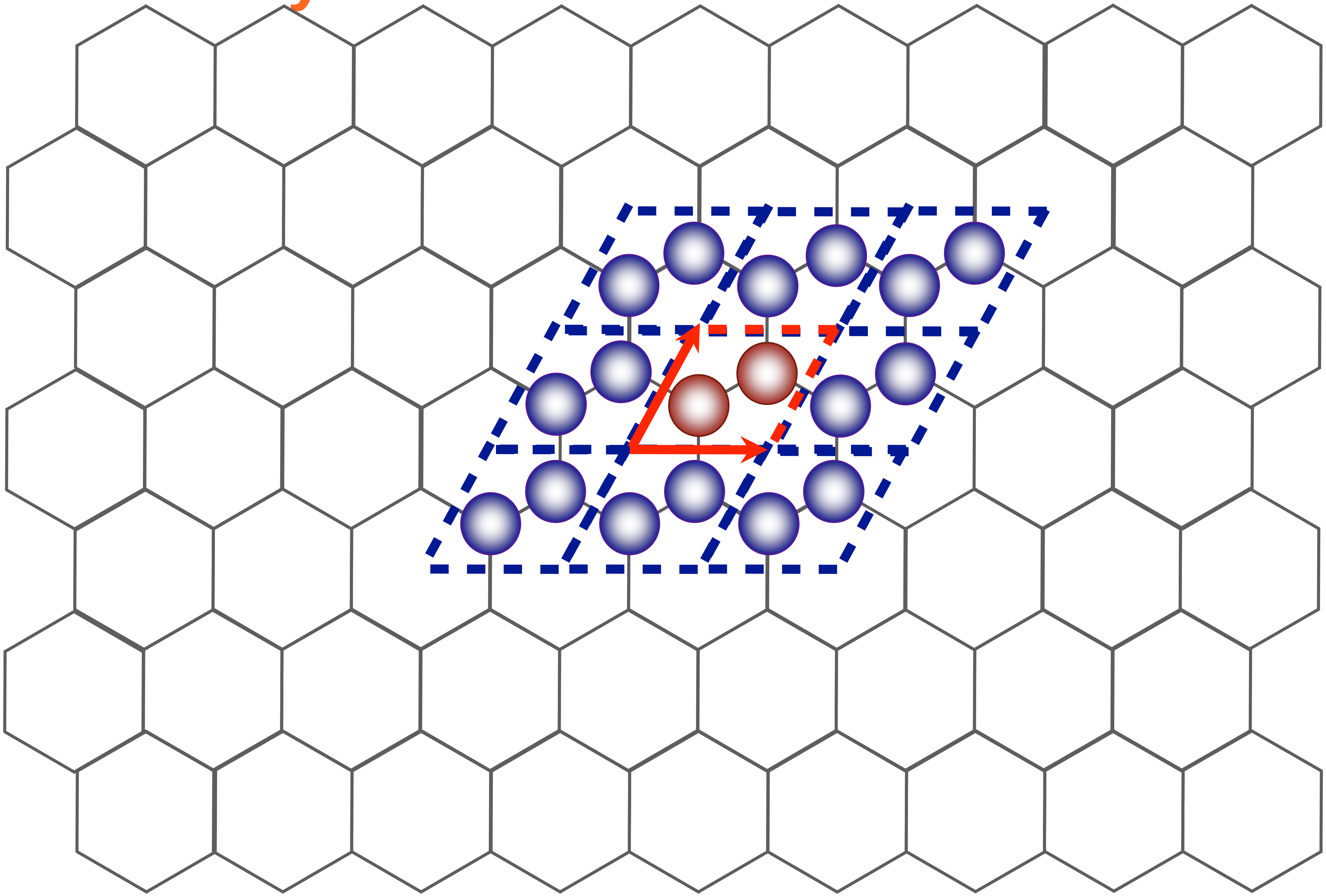
- Lattice vectors are not unique.
- Any linear combination works.



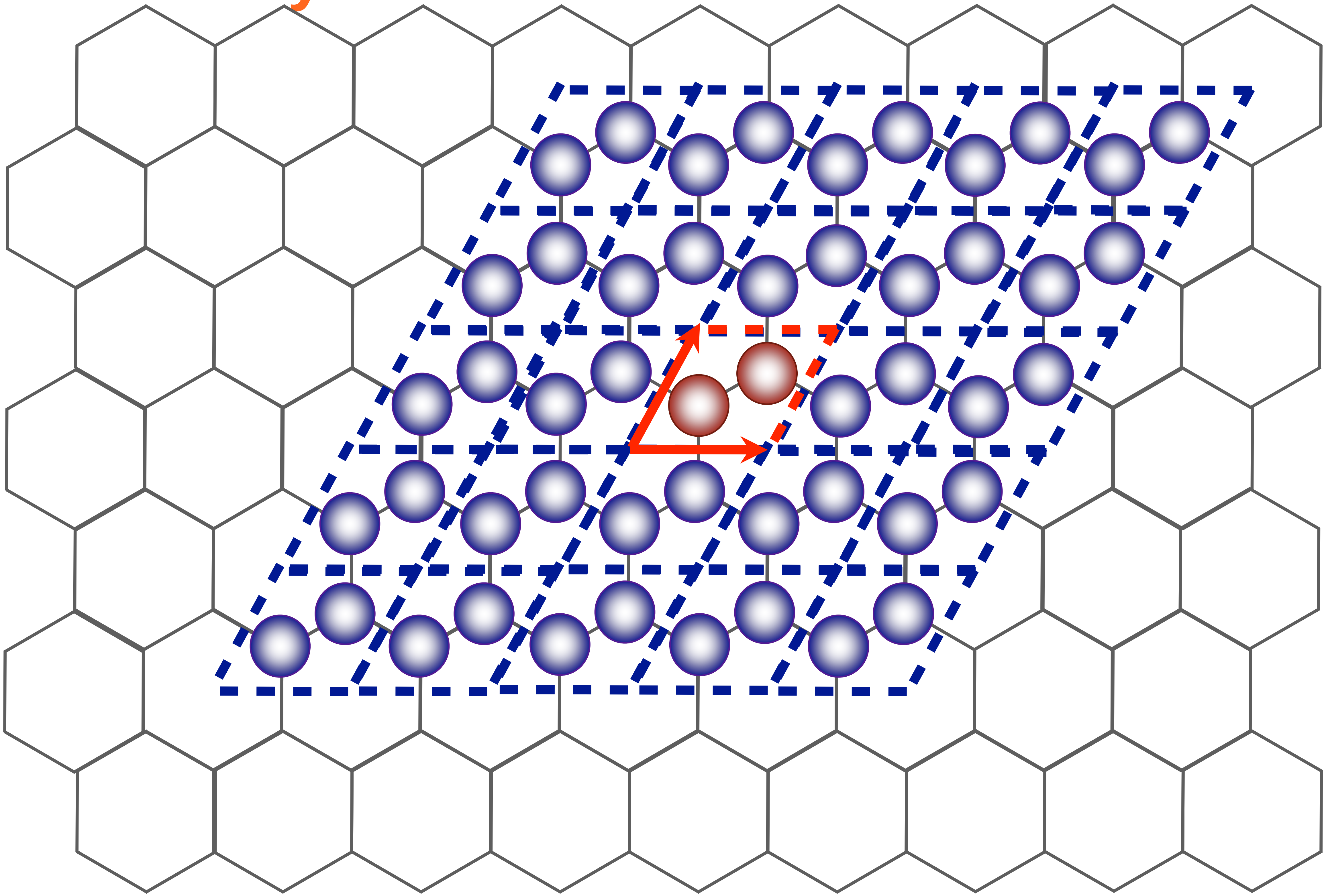
Periodic systems — basis



Periodic systems — basis



Periodic systems — basis



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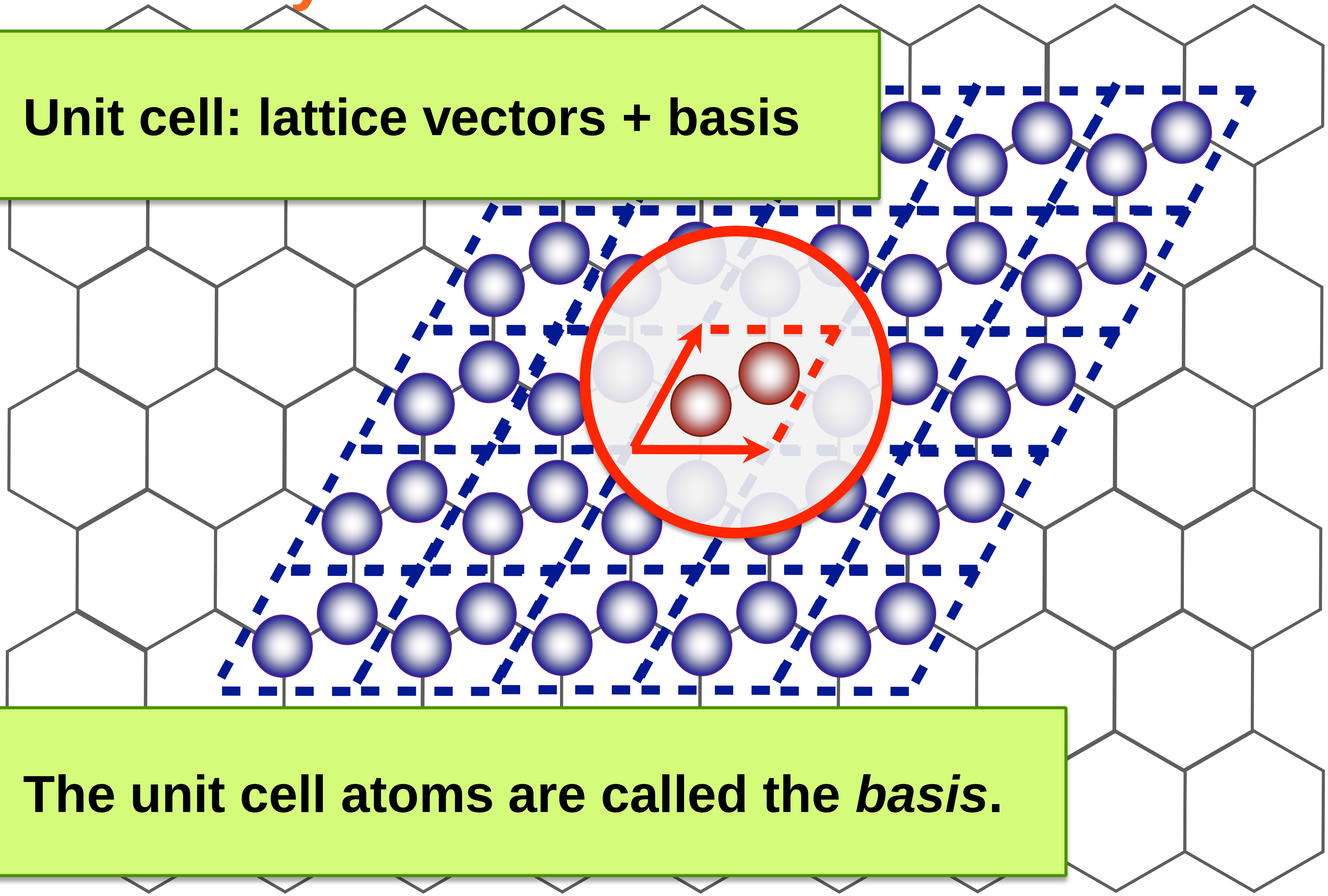
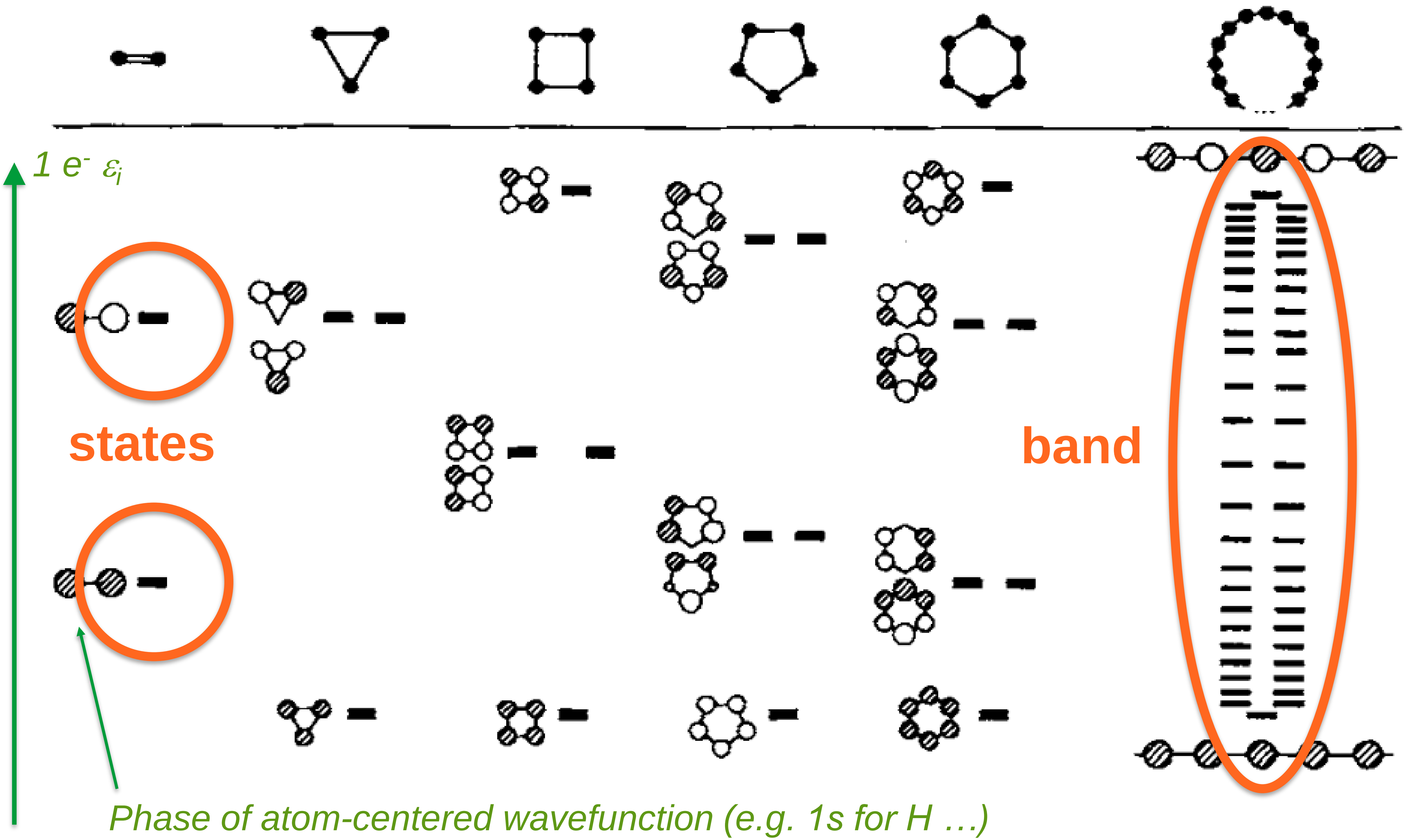
Periodic systems — unit cell



Unit cell: lattice vectors + basis

The unit cell atoms are called the *basis*.

From molecules to solids again



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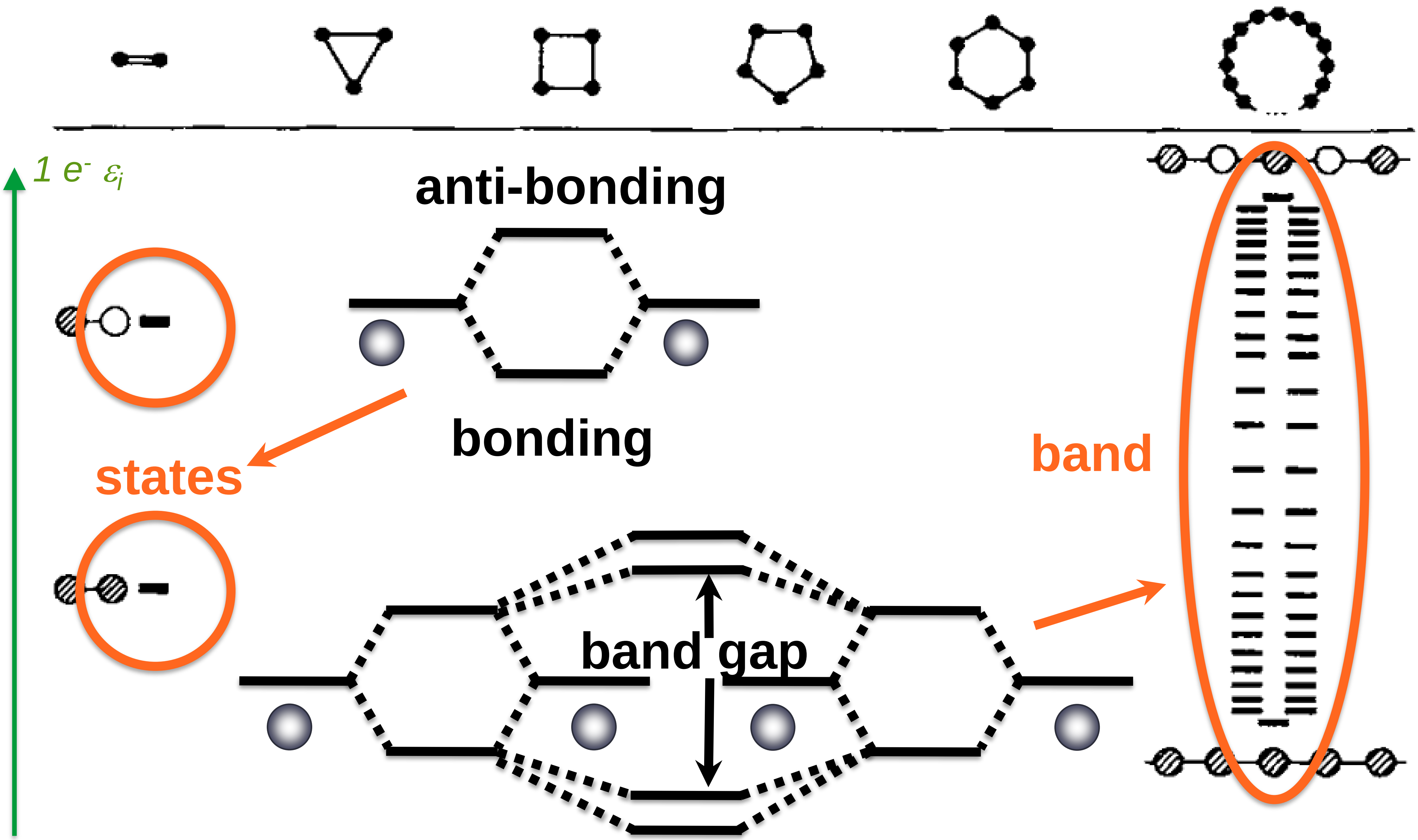
How Chemistry and Physics Meet in the Solid State, Roald Hoffmann, Angewandte Chemie 26, 846 (1987)

From molecules to solids again



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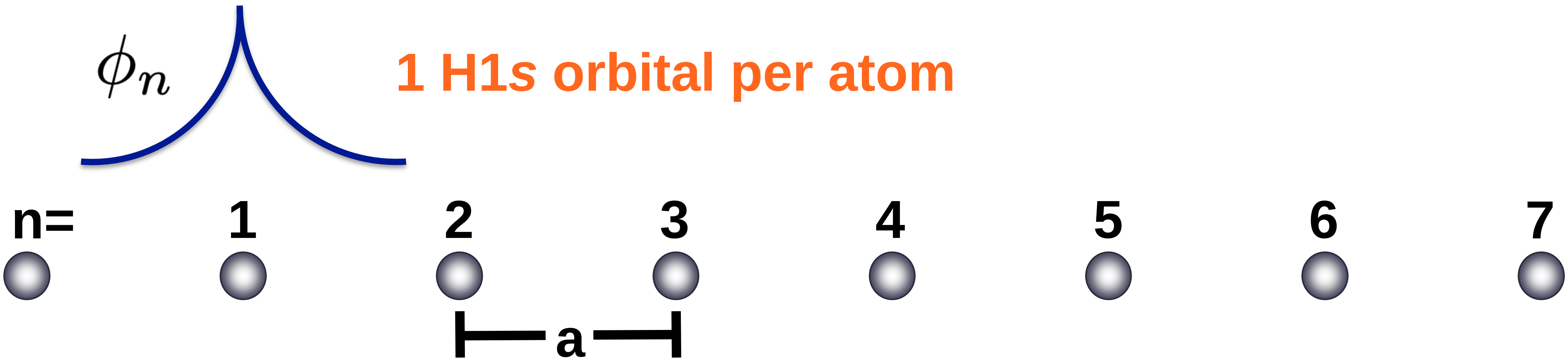
1D periodicity — Hydrogen chain



What will the wave function of the periodic chain be like?

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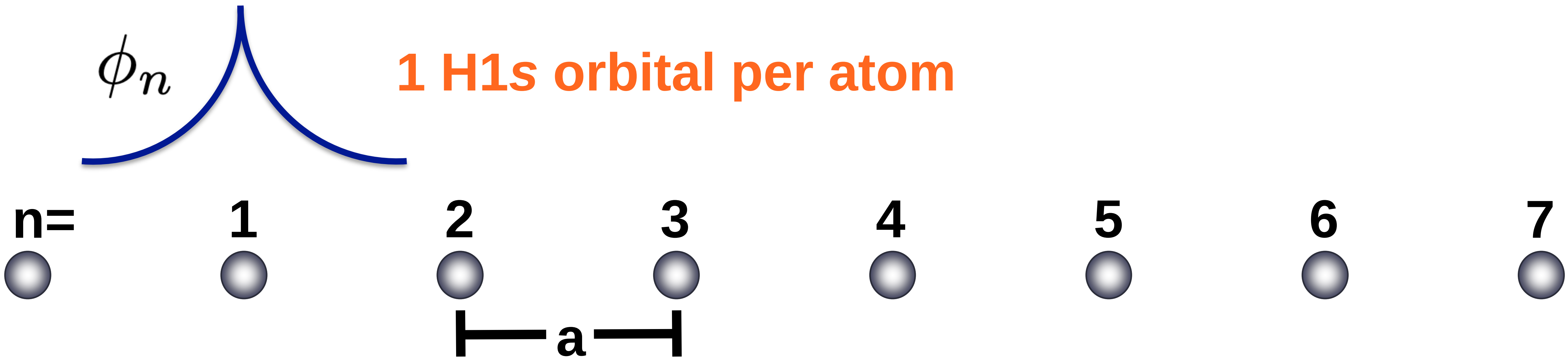
1D periodicity — Hydrogen chain

1 H1s orbital per atom



proper symmetrisation

$$\psi_k = \sum_n e^{ikna}\phi_n \qquad e^{ix} = \cos(x) + i\sin(x)$$

Still one electron wavefunction

***n*-nuclei centered 1s orbital**

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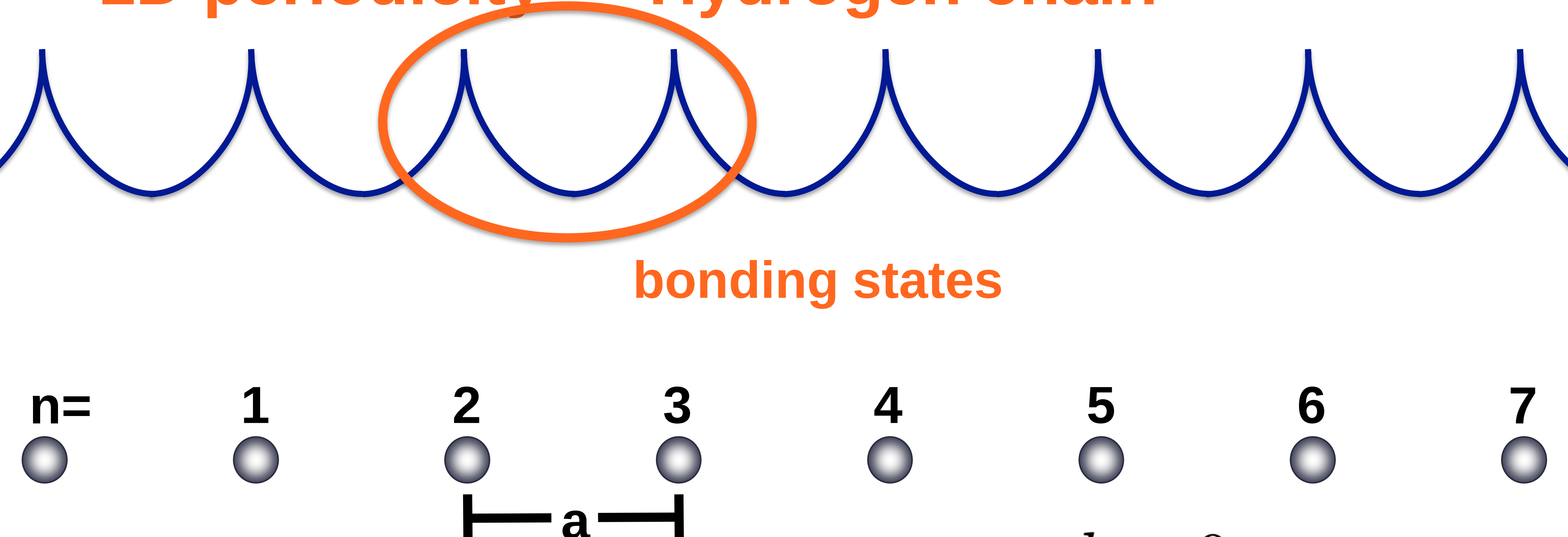
1D periodicity — Hydrogen chain



$k = 0$

$$\psi_k = \sum_n e^{ikna} \phi_n = \sum_n \phi_n$$

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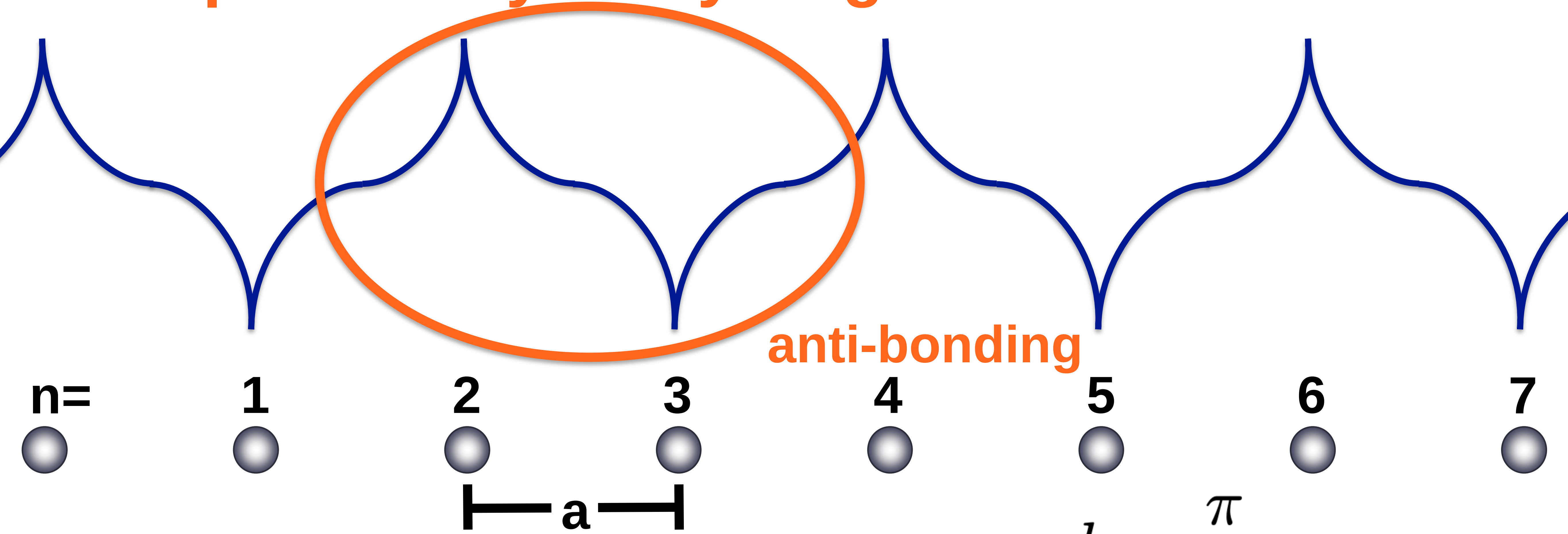
1D periodicity — Hydrogen chain



$$k = \frac{\pi}{a}$$

$$\psi_k = \sum_n e^{ikna}\phi_n = \sum_n (-1)^n \phi_n$$

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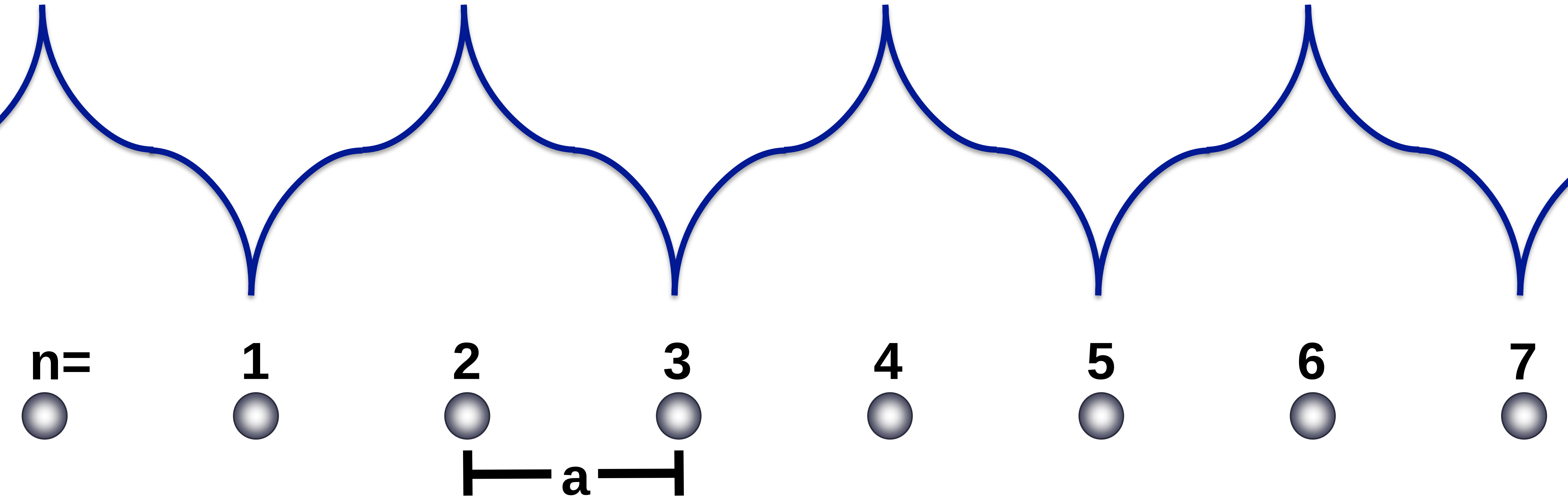
1D periodicity — Hydrogen chain



phase factor

$$\psi_k = \sum_n \boxed{e^{ikna}}\,\boxed{\phi_n}$$

lattice periodic

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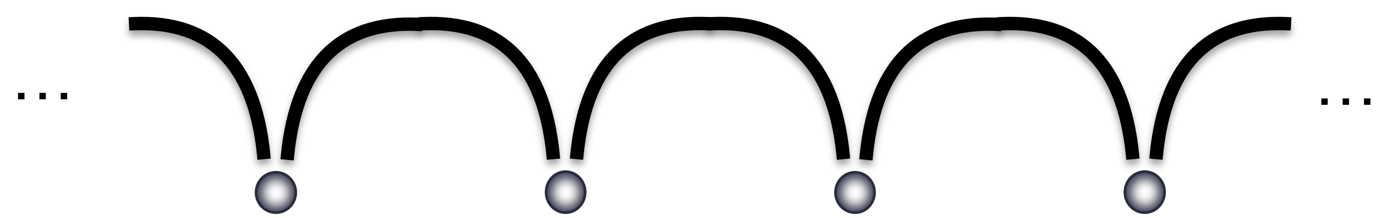
Bloch Theorem

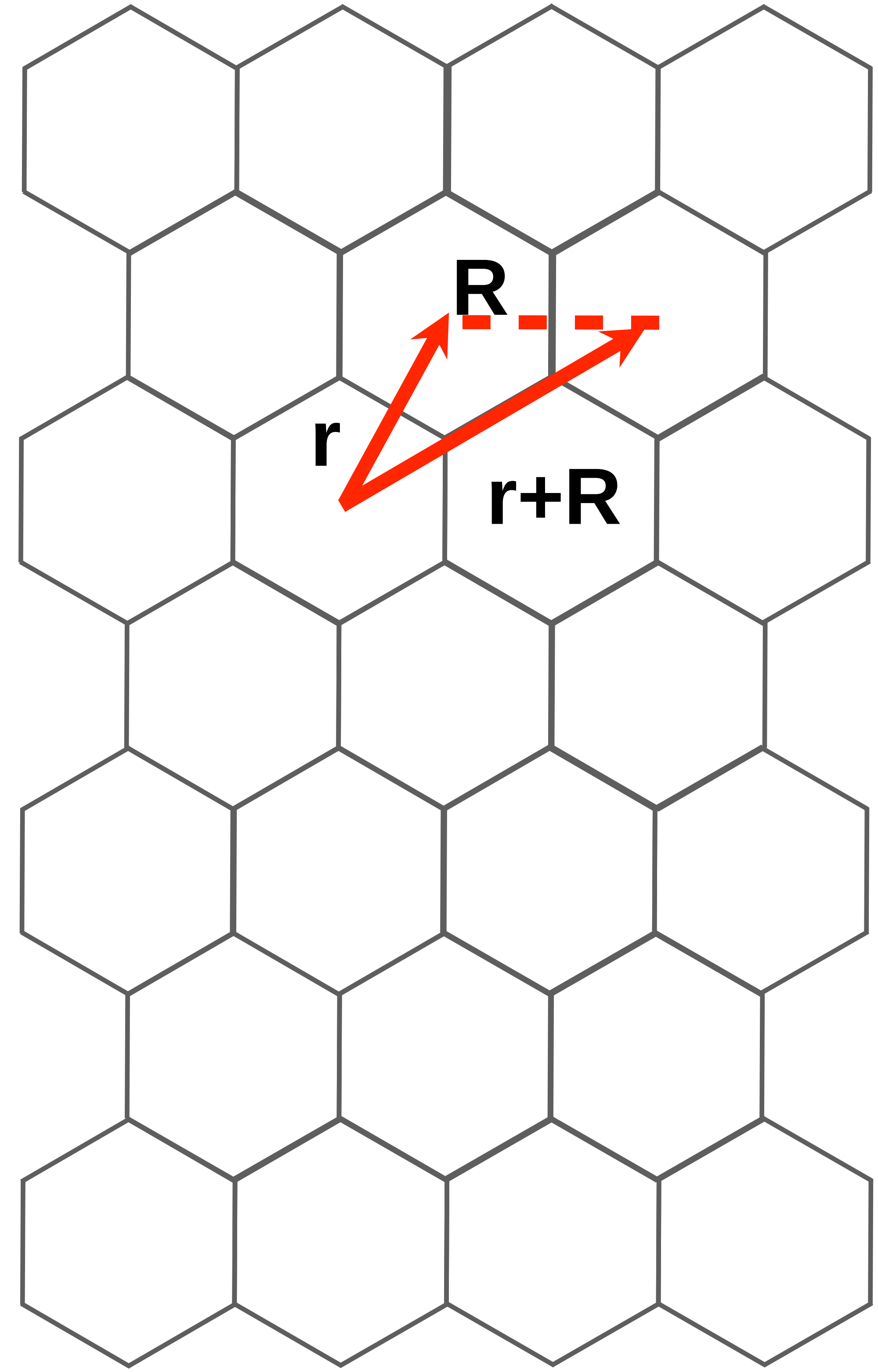
periodic potential:
(translational symmetry)

$$U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$$

R is one of our lattice vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$





Bloch Theorem

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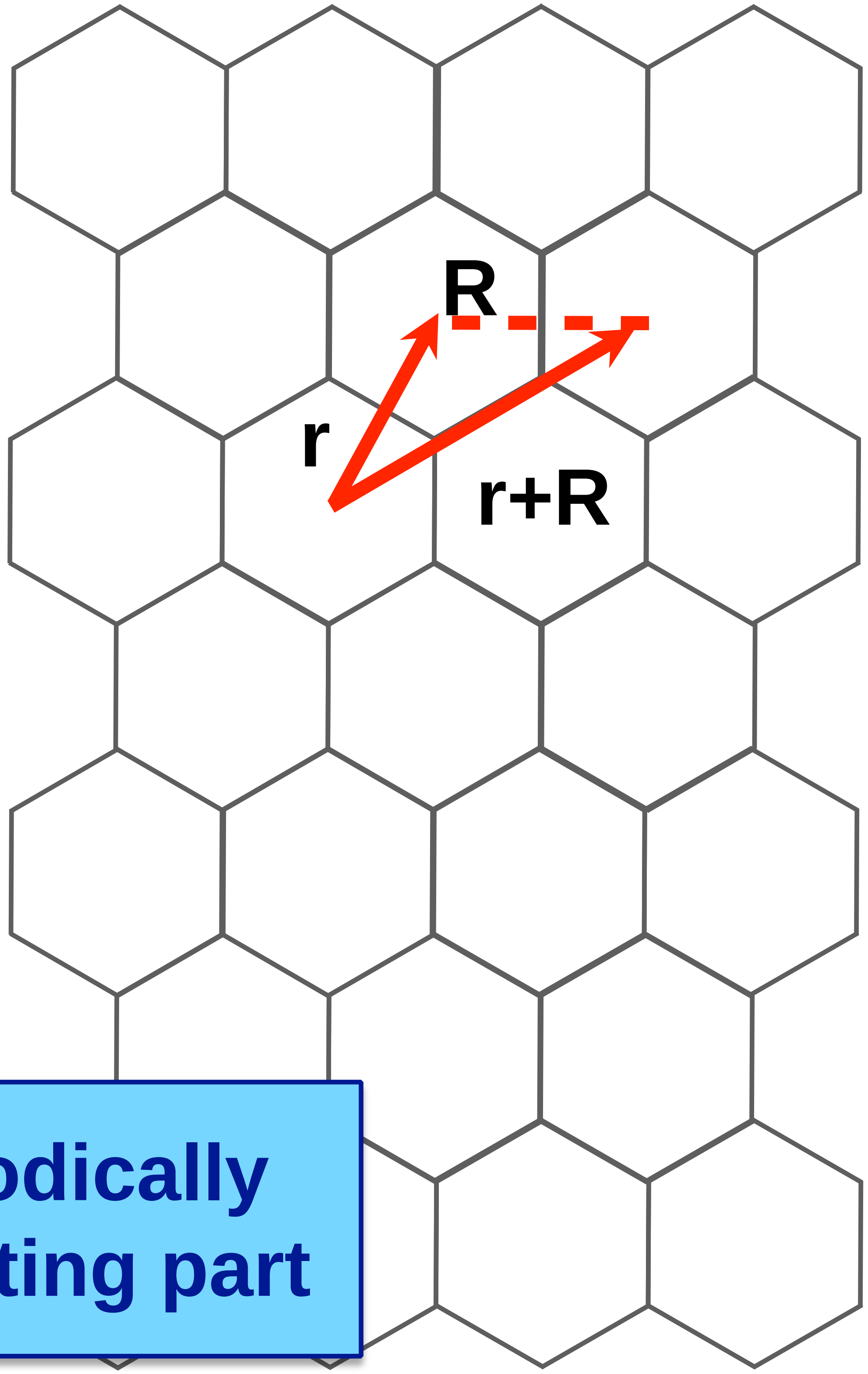
then also the wave function has to have a periodic part:

Still 1 e^- wave-function

$$\psi(\mathbf{r}) = e^{i\mathbf{kr}}u(\mathbf{r})$$

$$\boxed{u(\mathbf{r}+\mathbf{R}) = u(\mathbf{r})}$$

Periodically repeating part



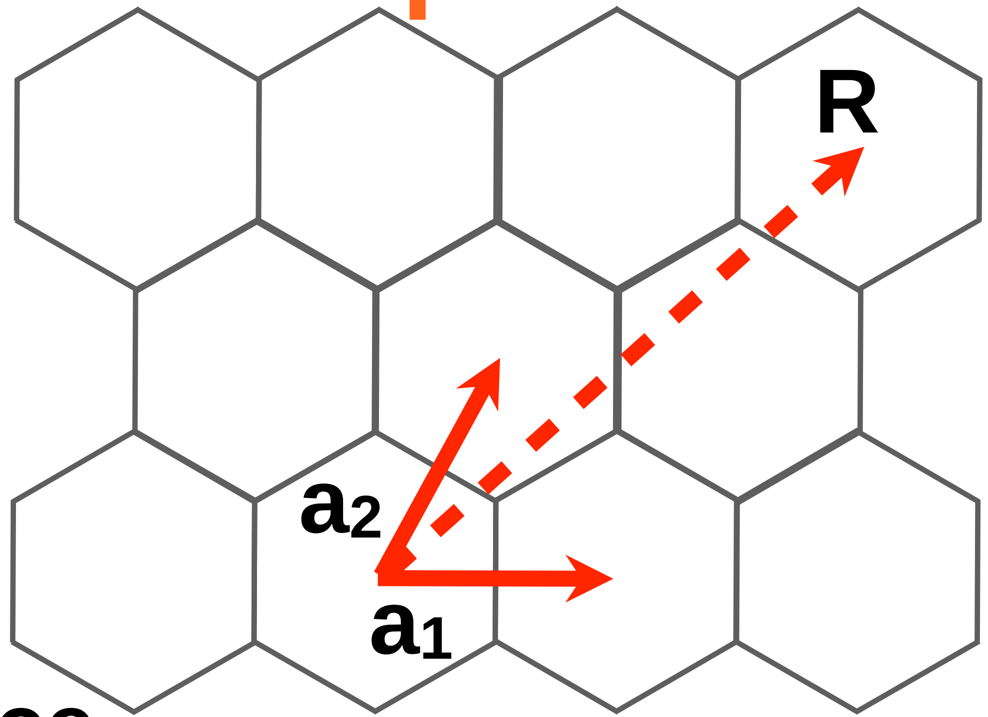
Bloch Theorem and reciprocal space

R is one of our lattice vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

$$\psi(\mathbf{r}) = e^{i\mathbf{kr}}u(\mathbf{r})$$

1 e^- wavefunction



real space

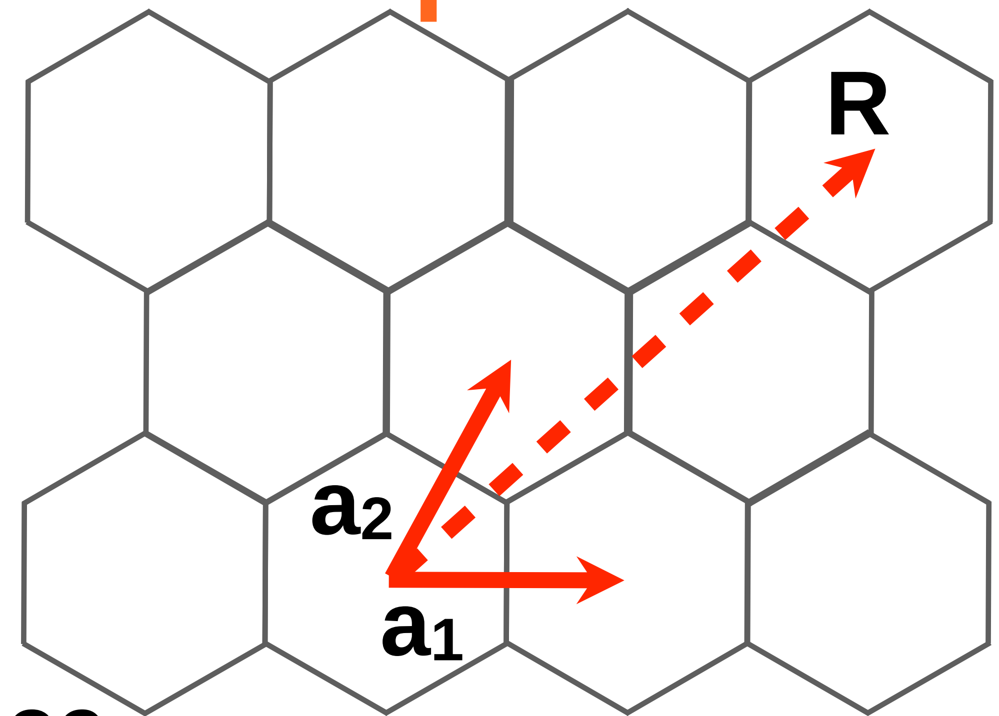
What is the *k*-vector?
Which values can *k* take?

Bloch Theorem and reciprocal space

R is one of our lattice vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

$$\psi(\mathbf{r}) = e^{i\mathbf{kr}}u(\mathbf{r})$$



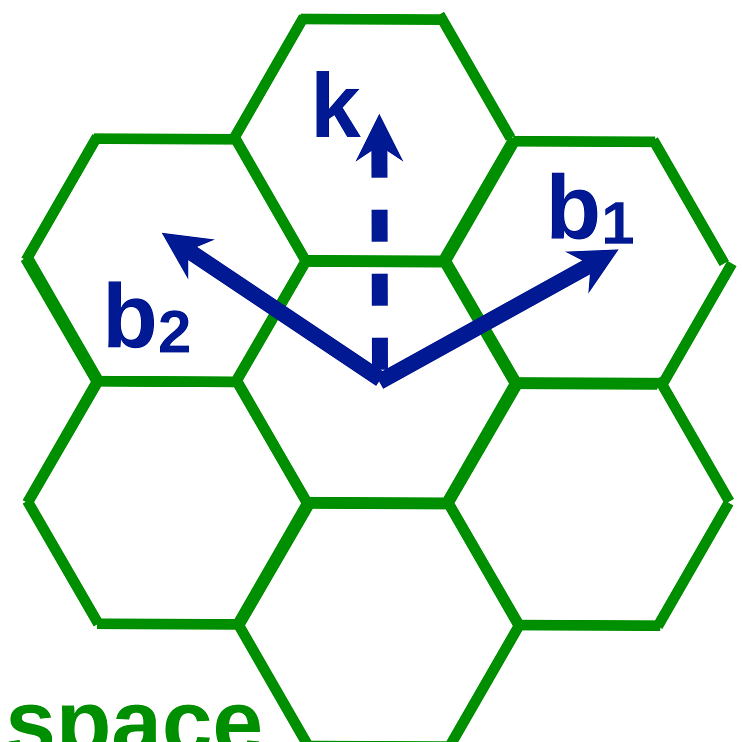
real space

reciprocal space:

$$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3$$

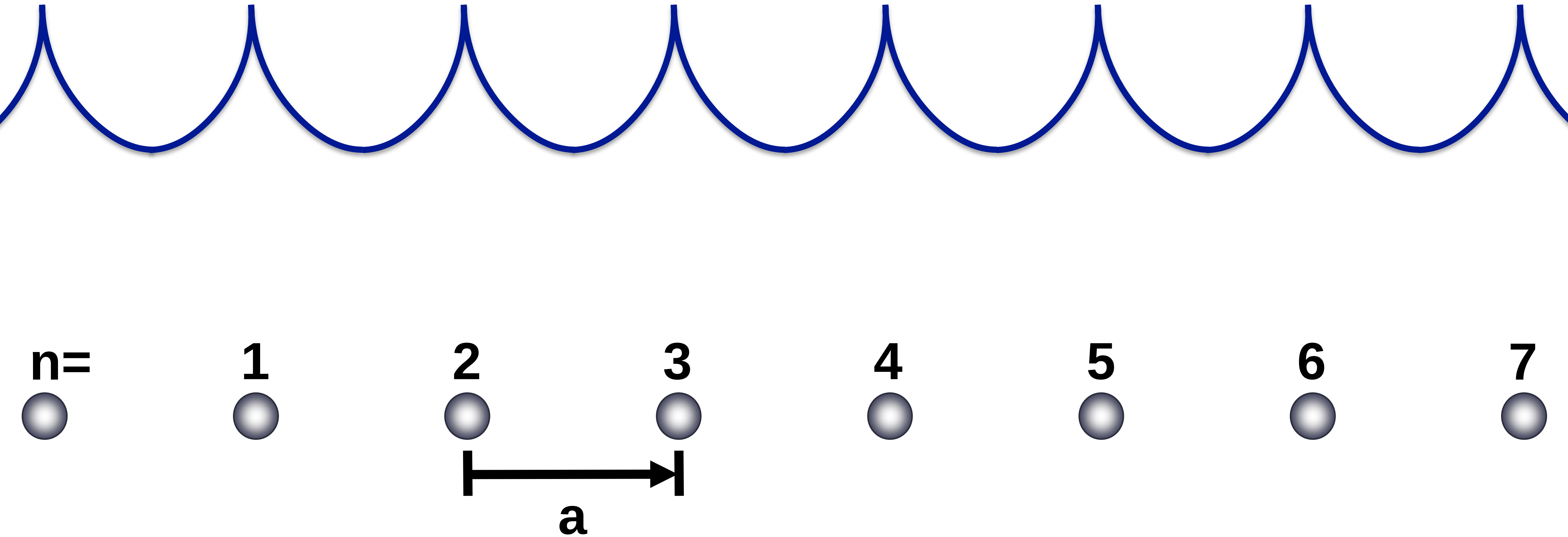
$$\mathbf{b}_i = \frac{2\pi}{\Omega}\mathbf{a}_j \times \mathbf{a}_l$$

unit cell volume



reciprocal space

1D periodicity — reciprocal space



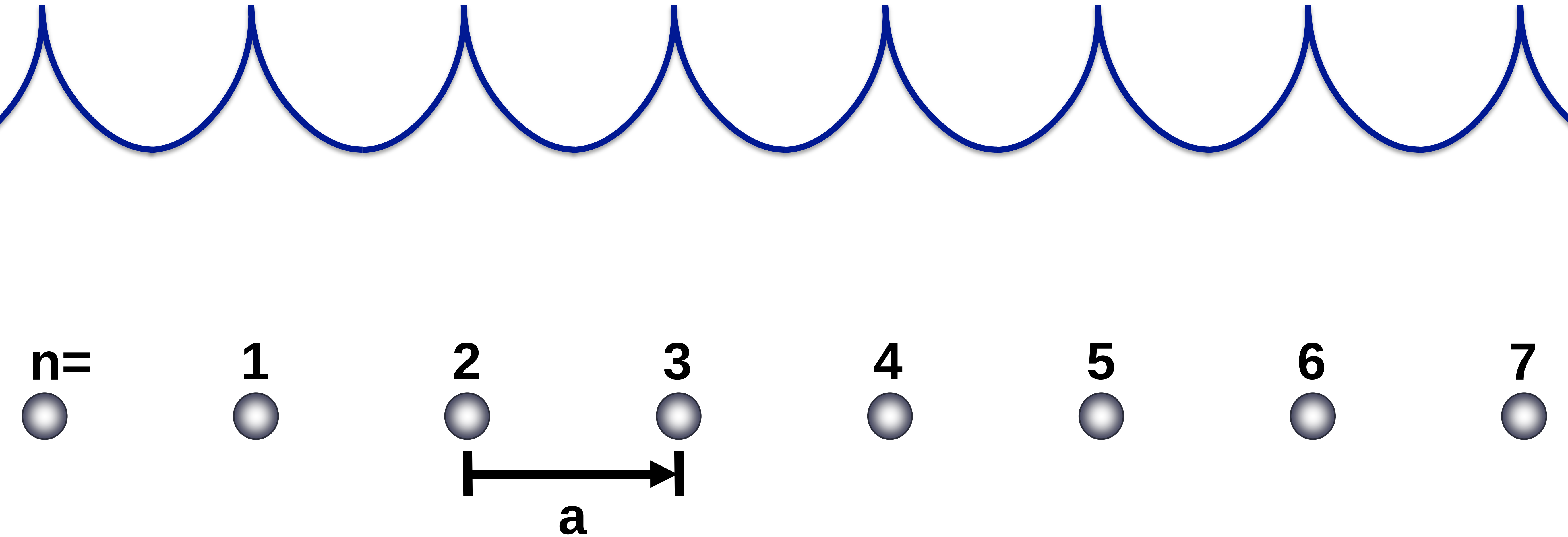
1 e$^-$
wavefunction

$$\psi_k = \sum_n e^{ikna}\phi_n$$

$$e^{ix} = \cos(x) + i\sin(x)$$

Which values can *k* take?

1D periodicity — reciprocal space

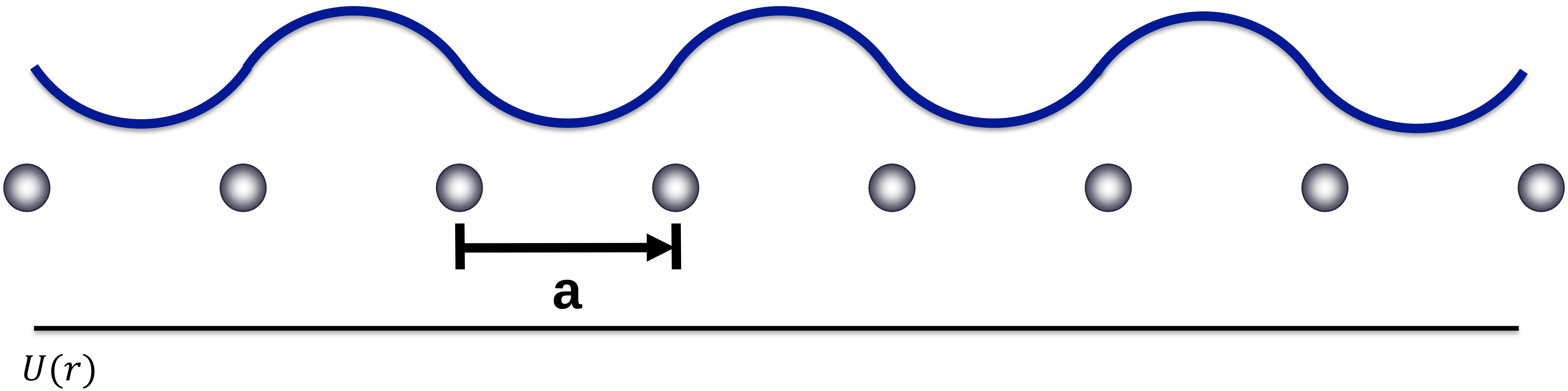


$$\psi_k = \sum_n e^{ikna}\phi_n \qquad e^{ix} = \cos(x) + i\sin(x)$$

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a}$$ **then exp. repeats itself**

Flat potential — “1D metal”

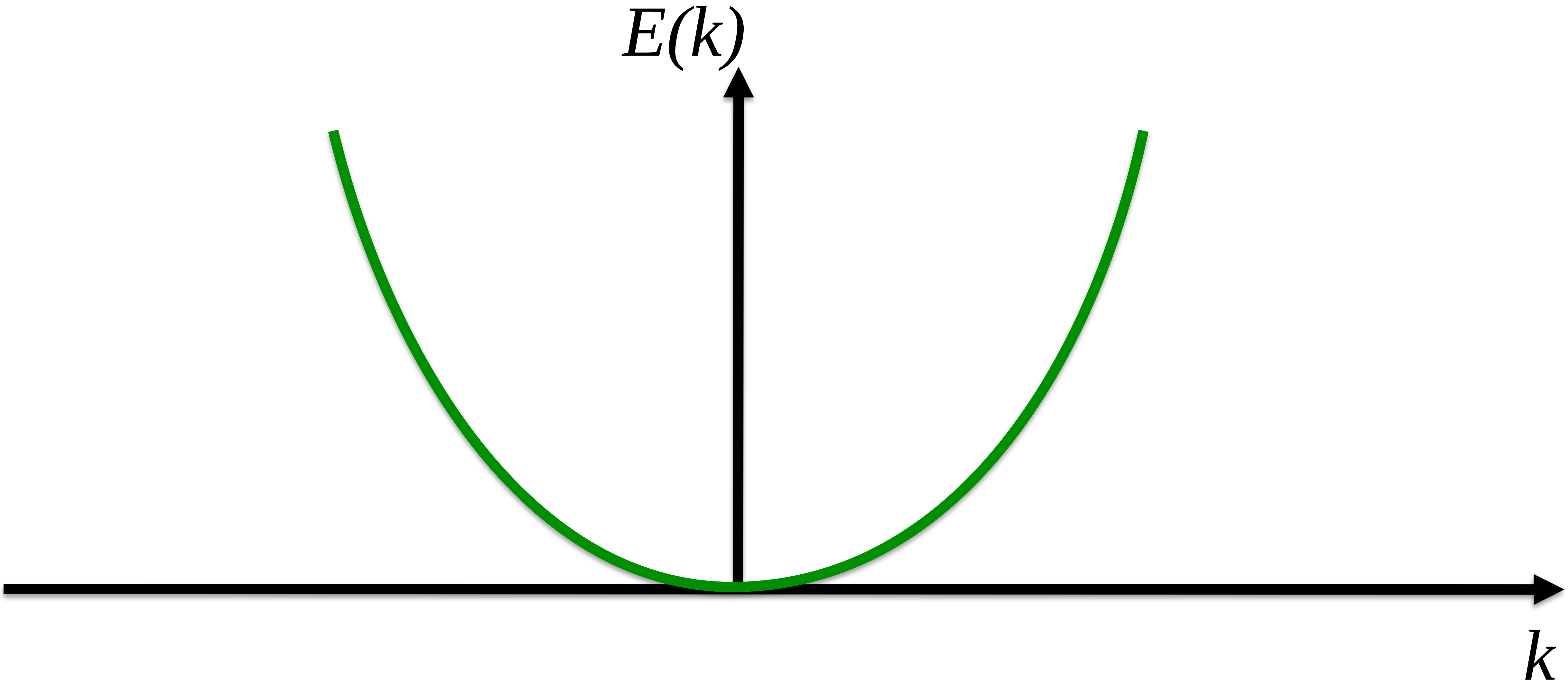
$$U(r+a) = U(r) = \text{constant}$$



Solution is a plane wave:

$$\phi(r) = e^{ikr} \qquad E(k) = \frac{k^2}{2}$$

Flat potential — “1D metal”



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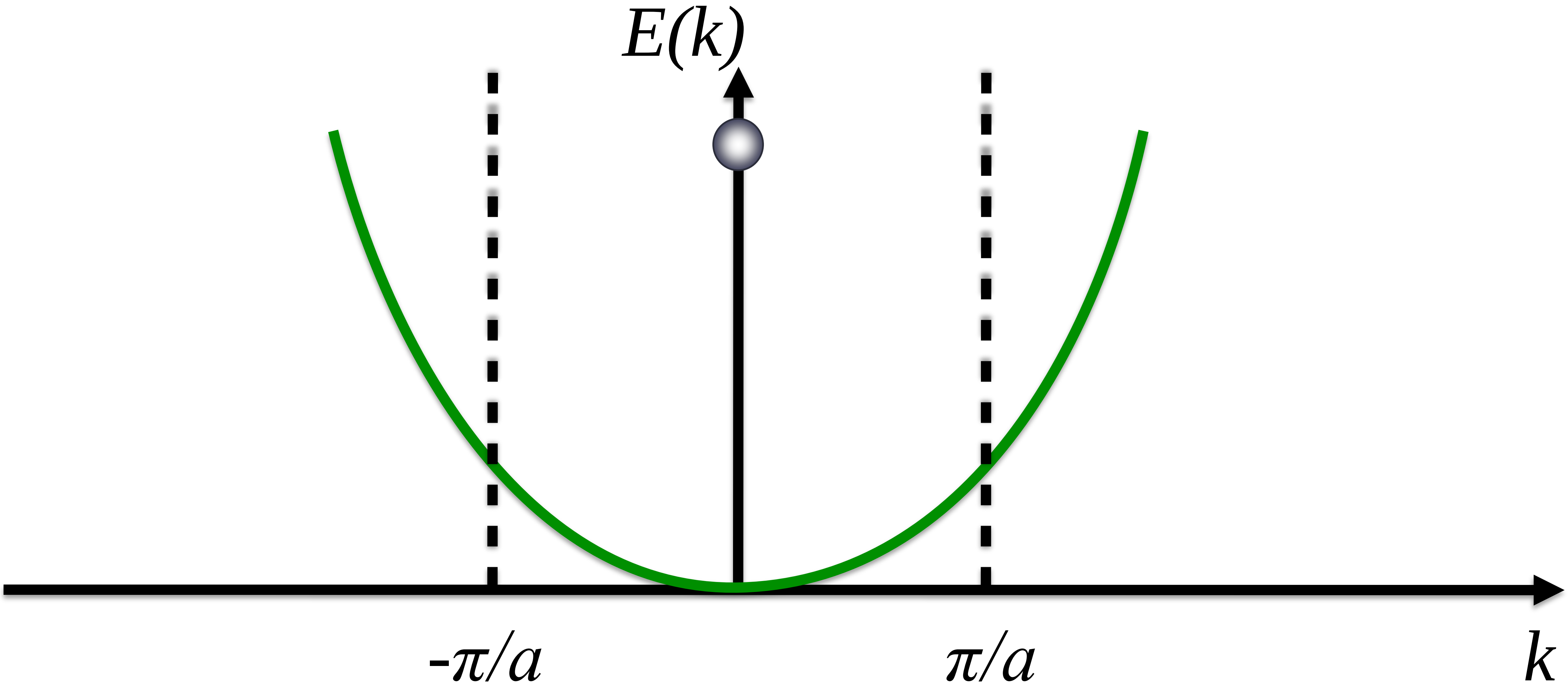
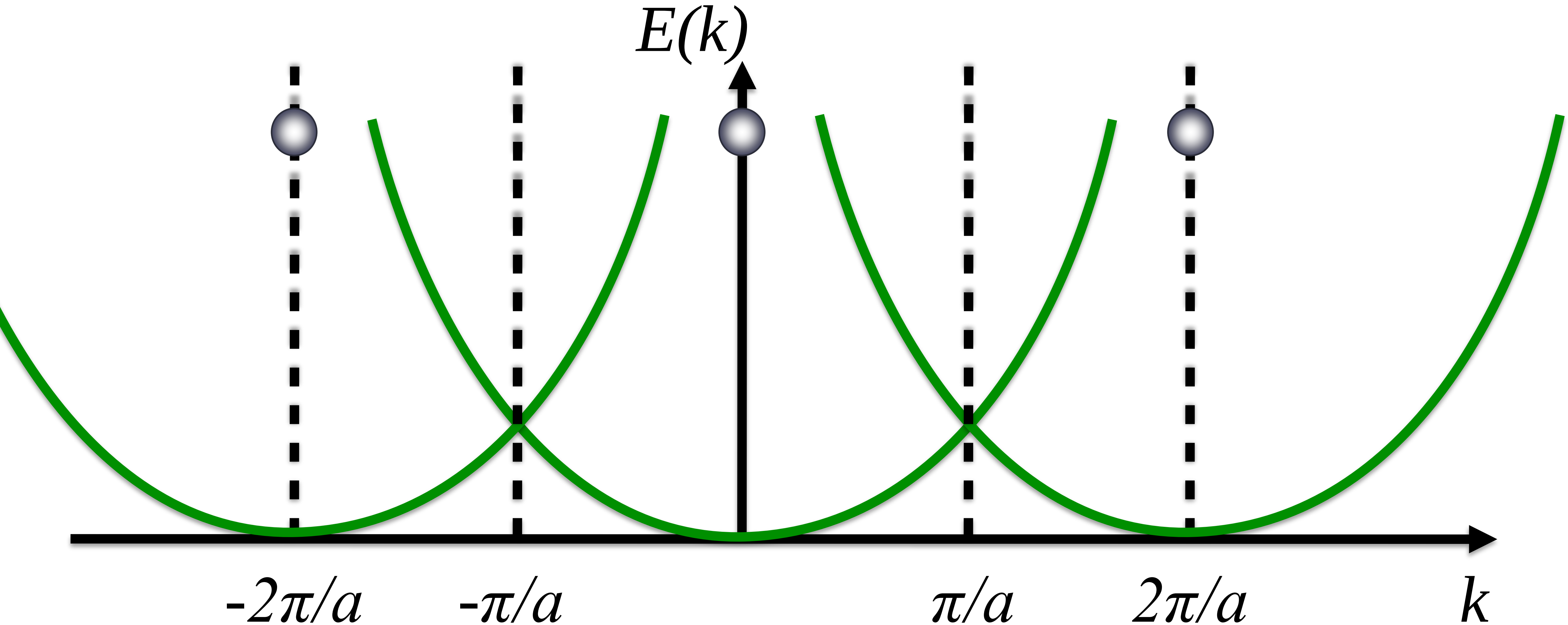


Solution is a plane wave:

$$\phi(r) = e^{ikr} \qquad E(k) = \frac{k^2}{2} \qquad -\frac{\pi}{a} < k \leq \frac{\pi}{a}$$

Flat potential — "1D metal"



Solution repeats itself

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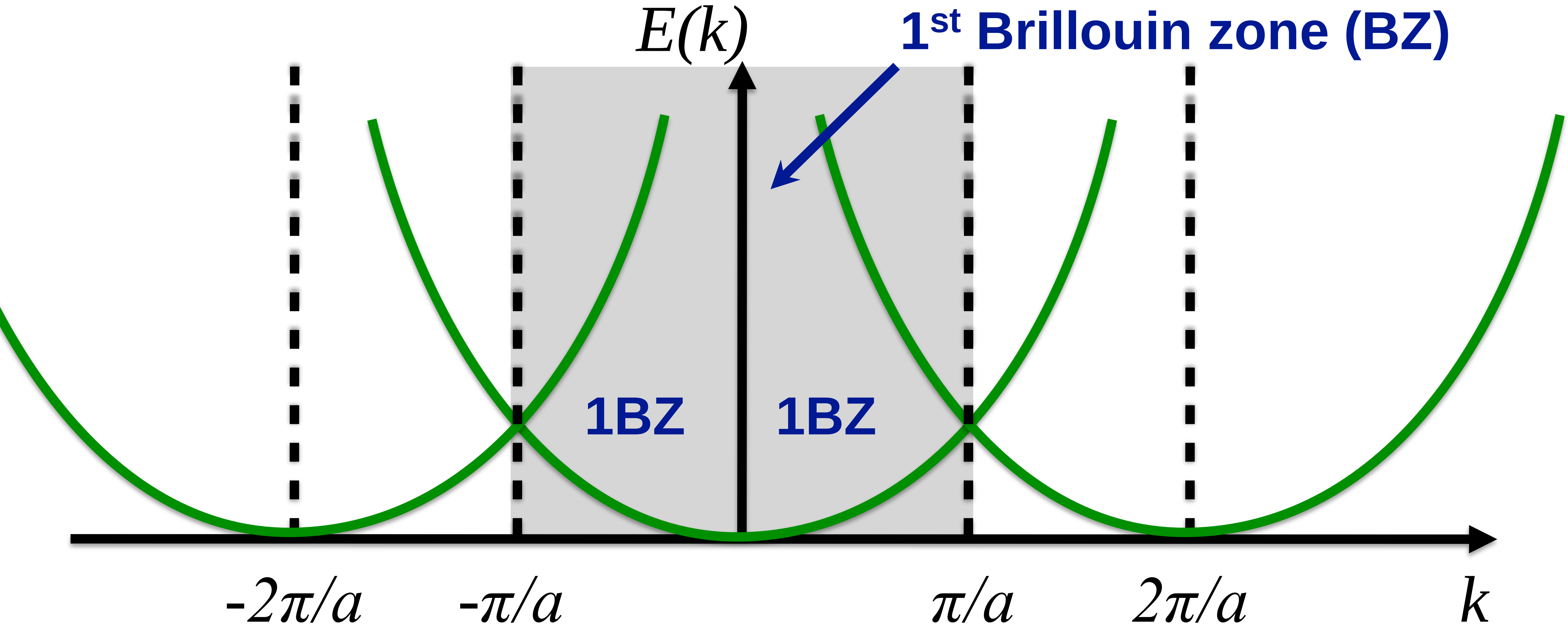
Flat potential — "1D metal"



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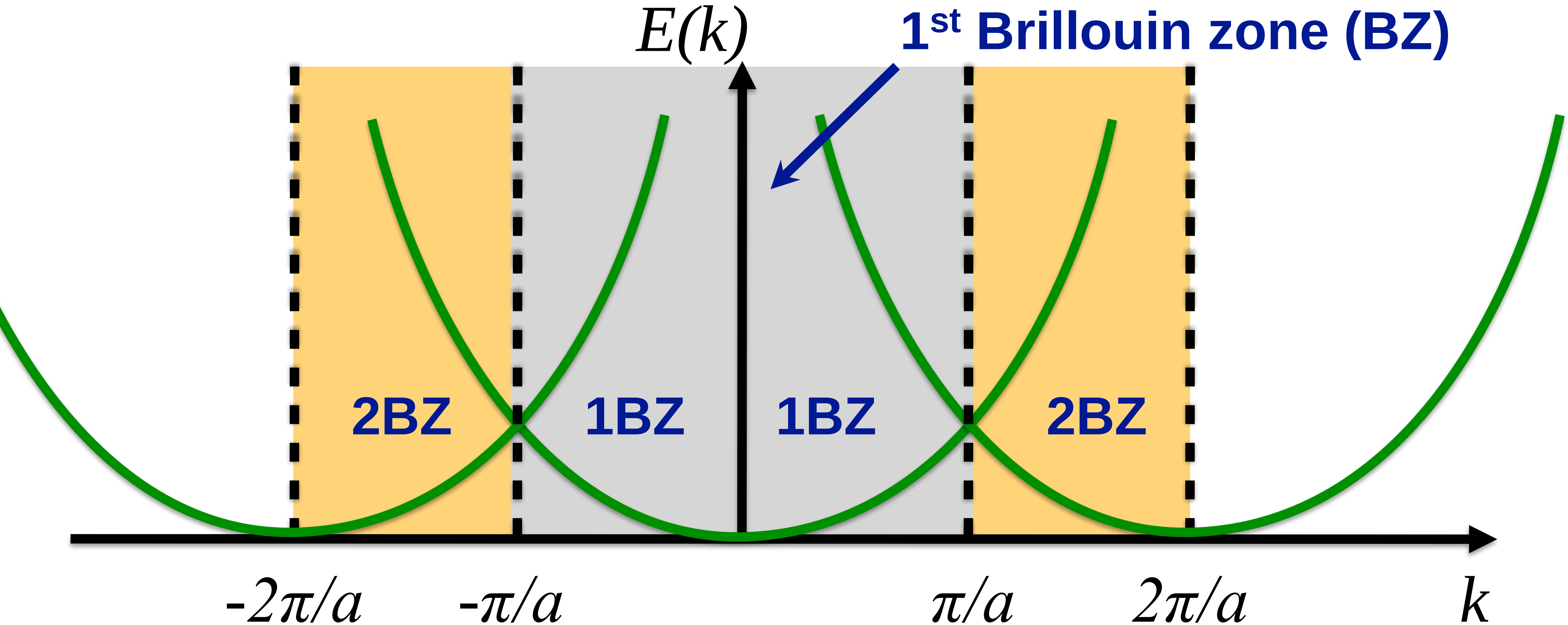

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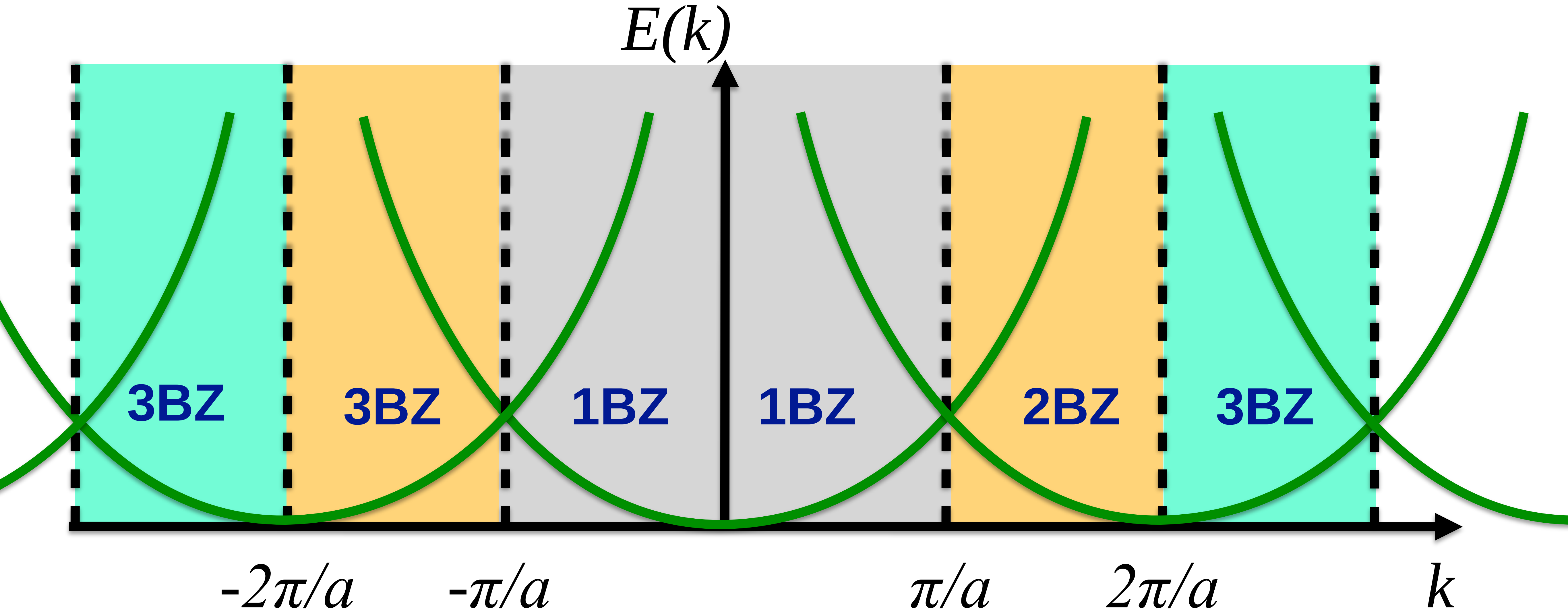
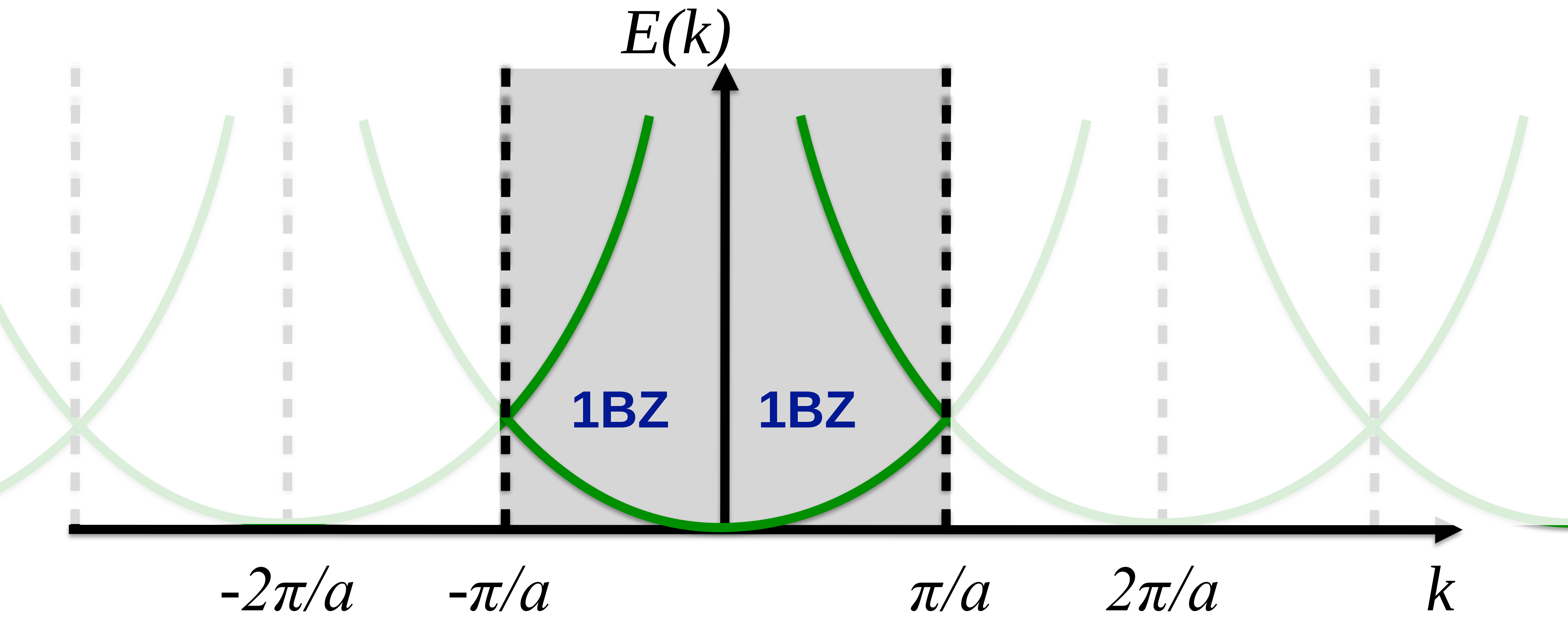
Flat potential — “1D metal”



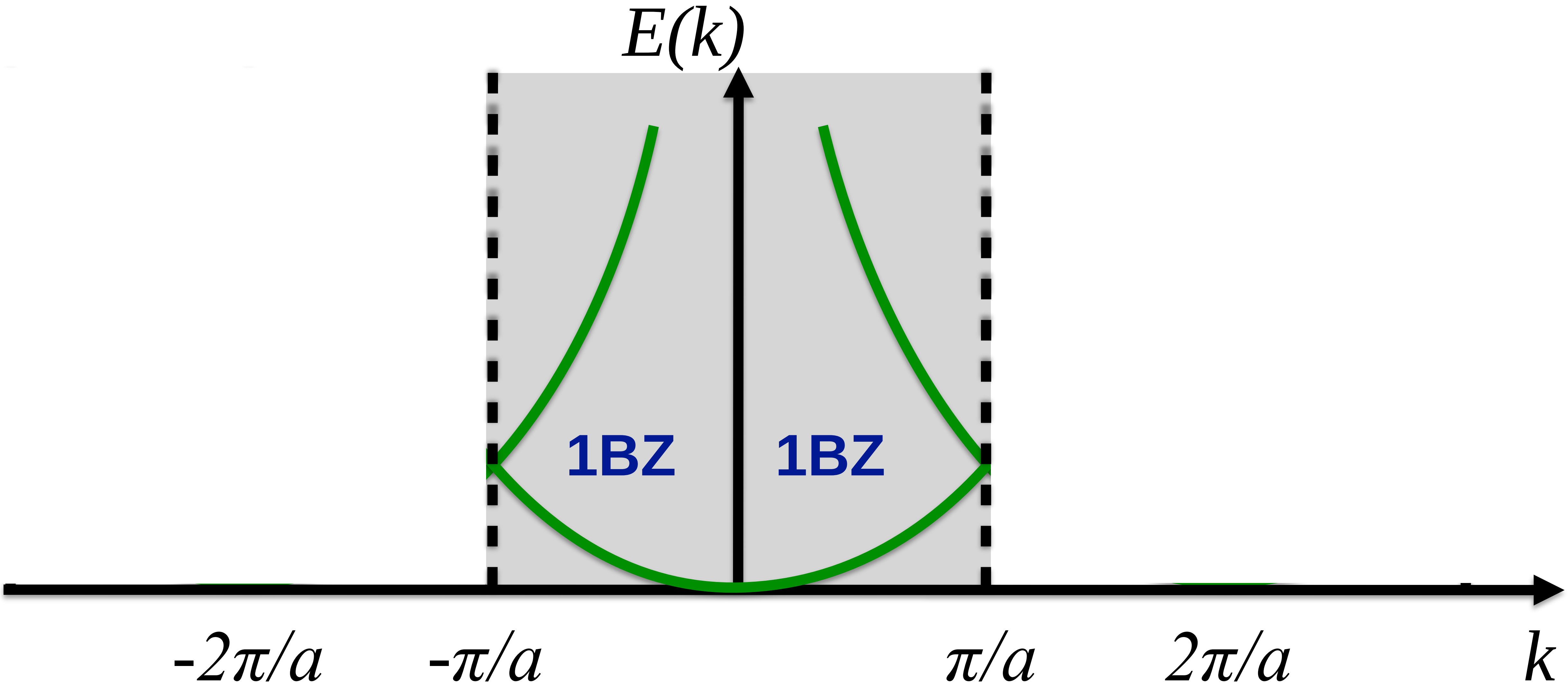
Extended zone scheme

Flat potential — “1D metal”



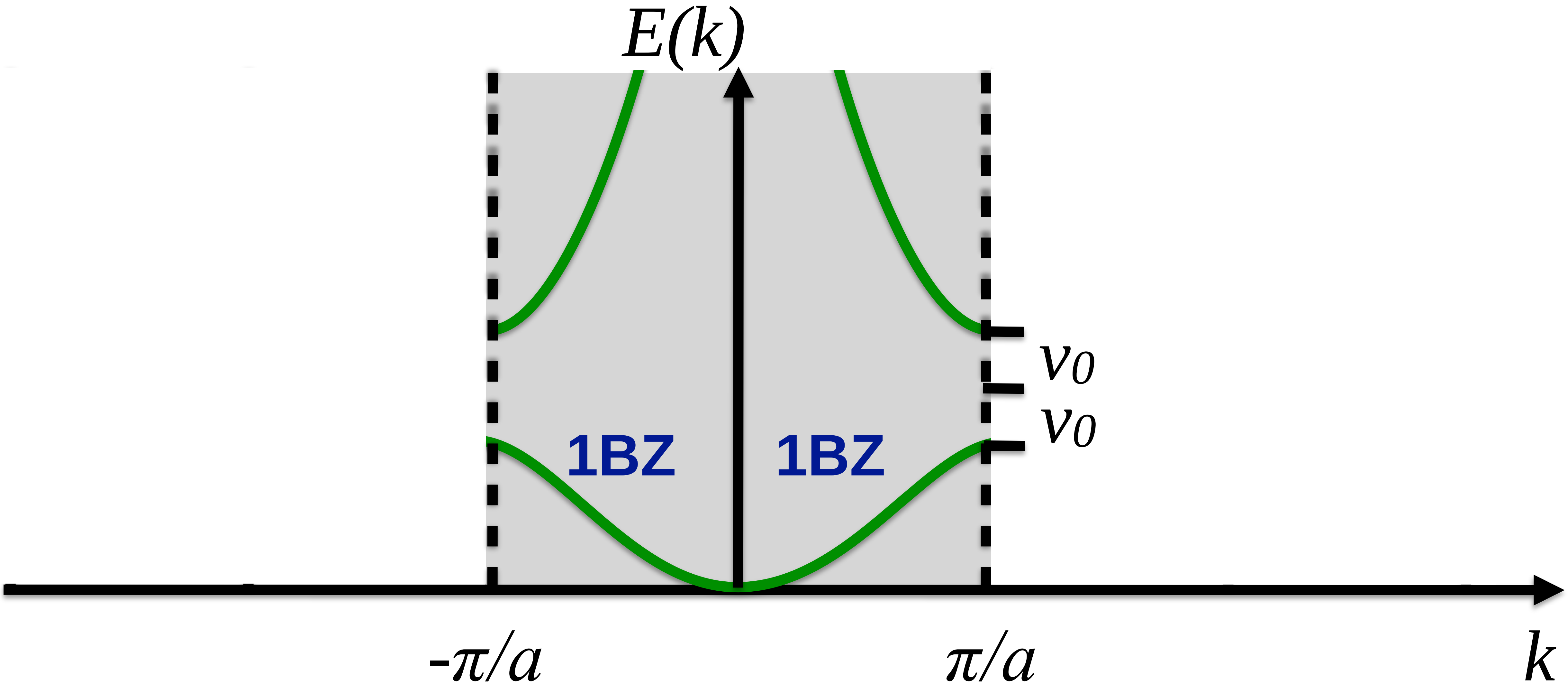
Reduced zone scheme

Flat potential — "1D metal"

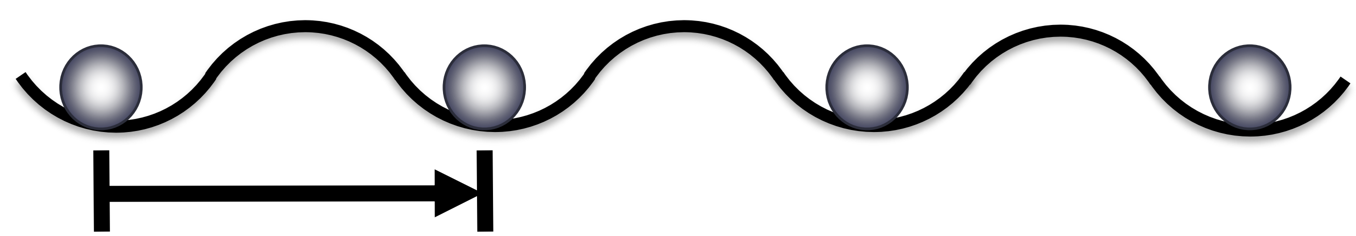


Reduced zone scheme

Periodic potential opens gap



$$v(r) = v_0 \cos(\pi \frac{r}{a})$$

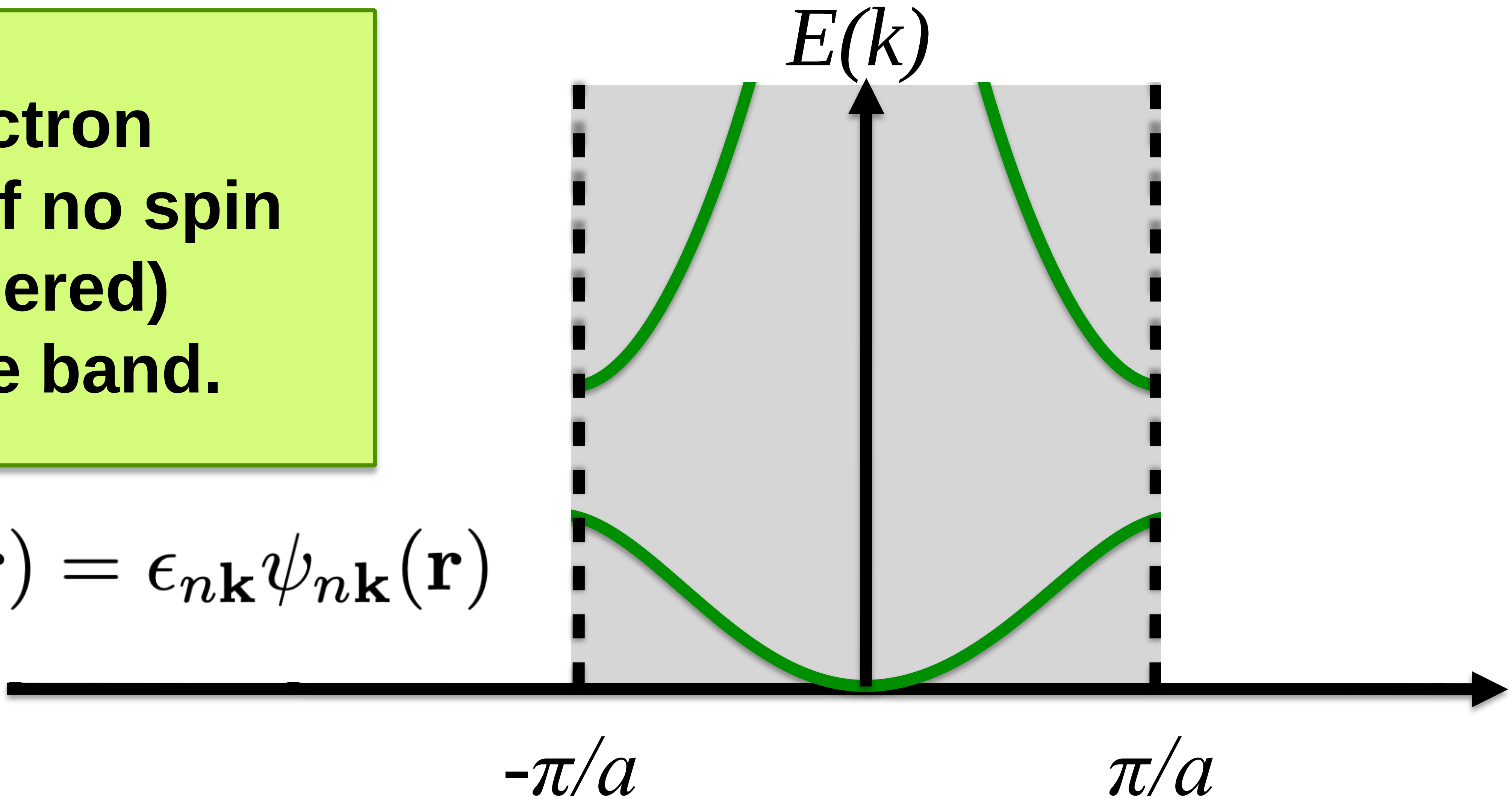


Summary

Each electron (or pair, if no spin is considered) gives one band.

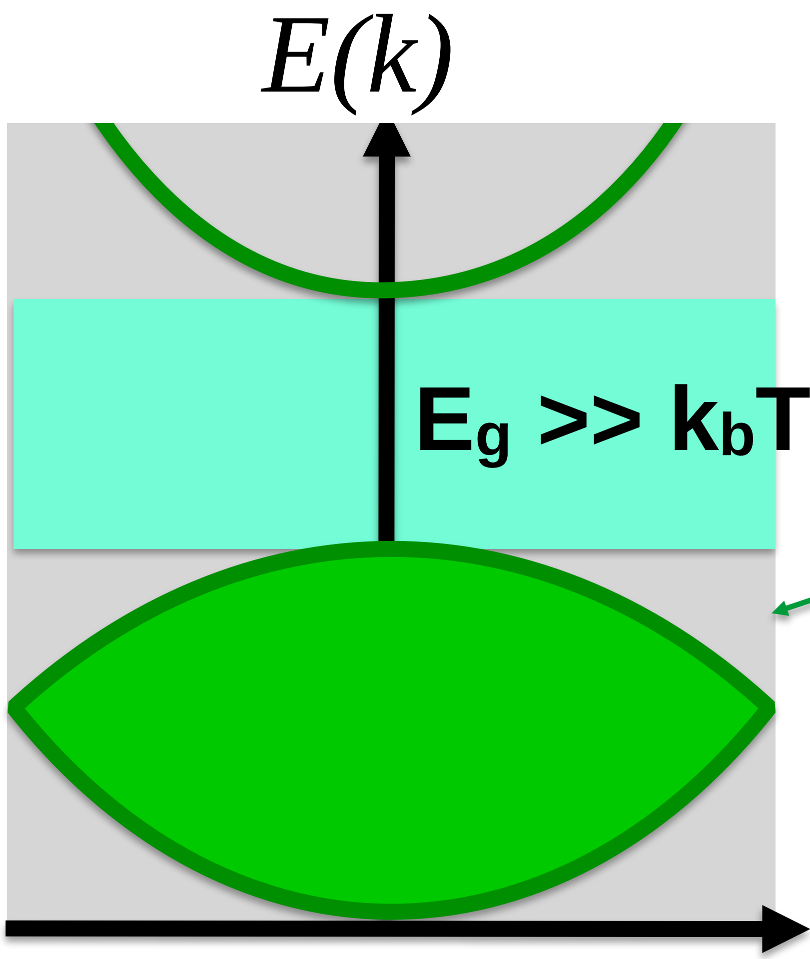
$$h_{\mathrm{aux}}\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

1 e$^-$ Hamiltonian & wavefunction



The Fermi energy marks the energy of the highest occupied state.

Fermi energy



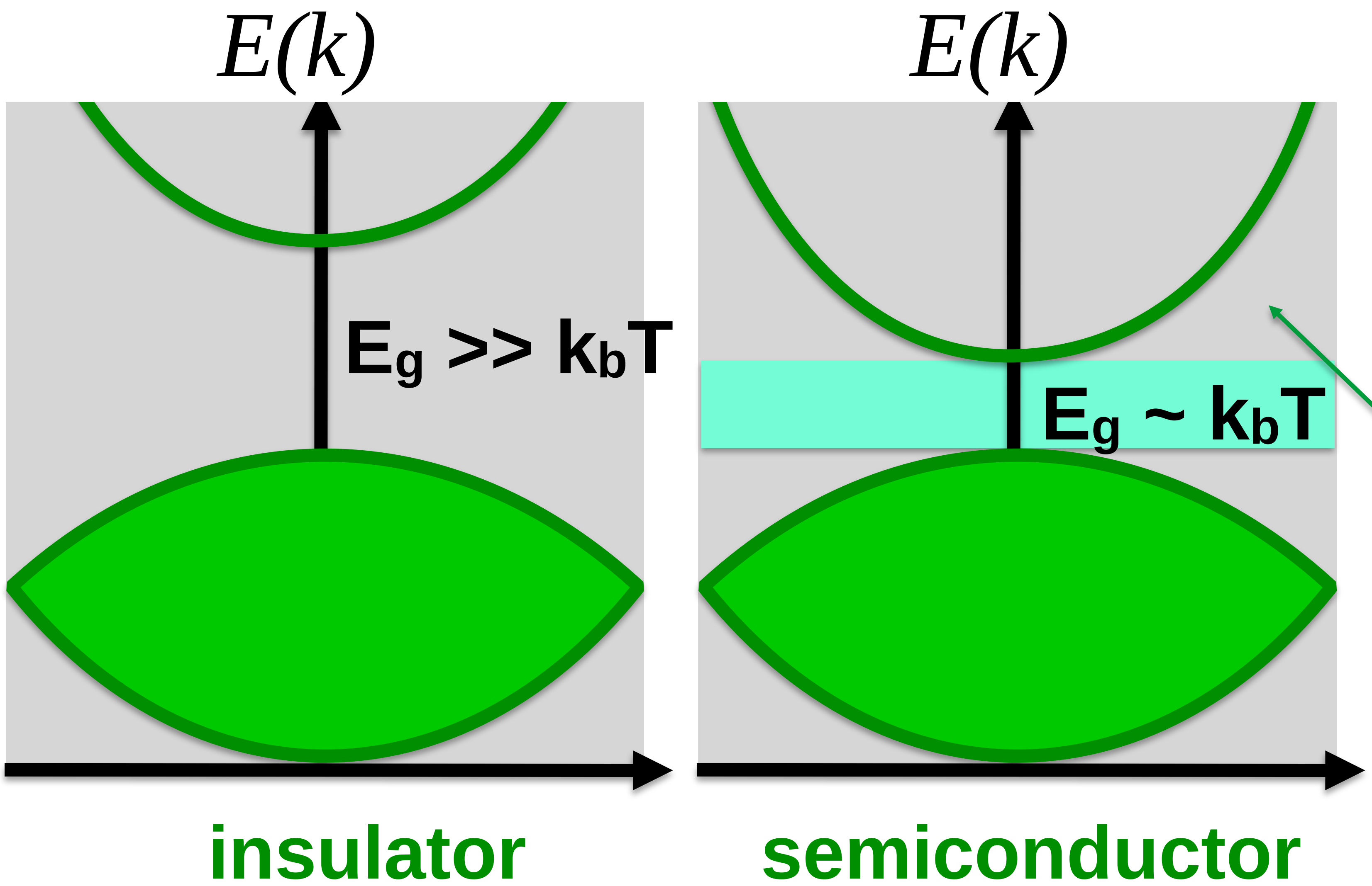
E_F ???

Fully occupied "valence" band

insulator

The Fermi energy marks the energy of the highest occupied state.

Fermi energy



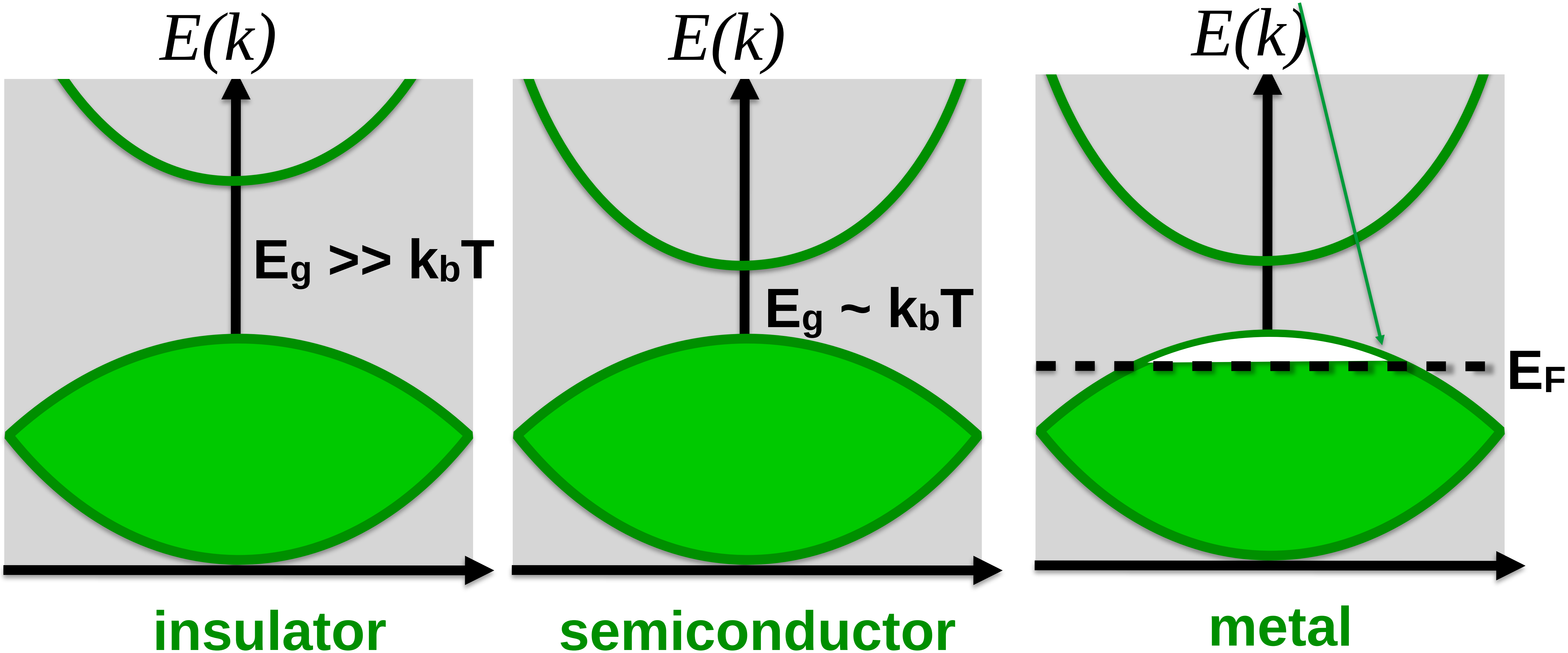
E_F ???

Non-occupied "conduction" band close to the valence band

The Fermi energy marks the energy of the highest occupied state.

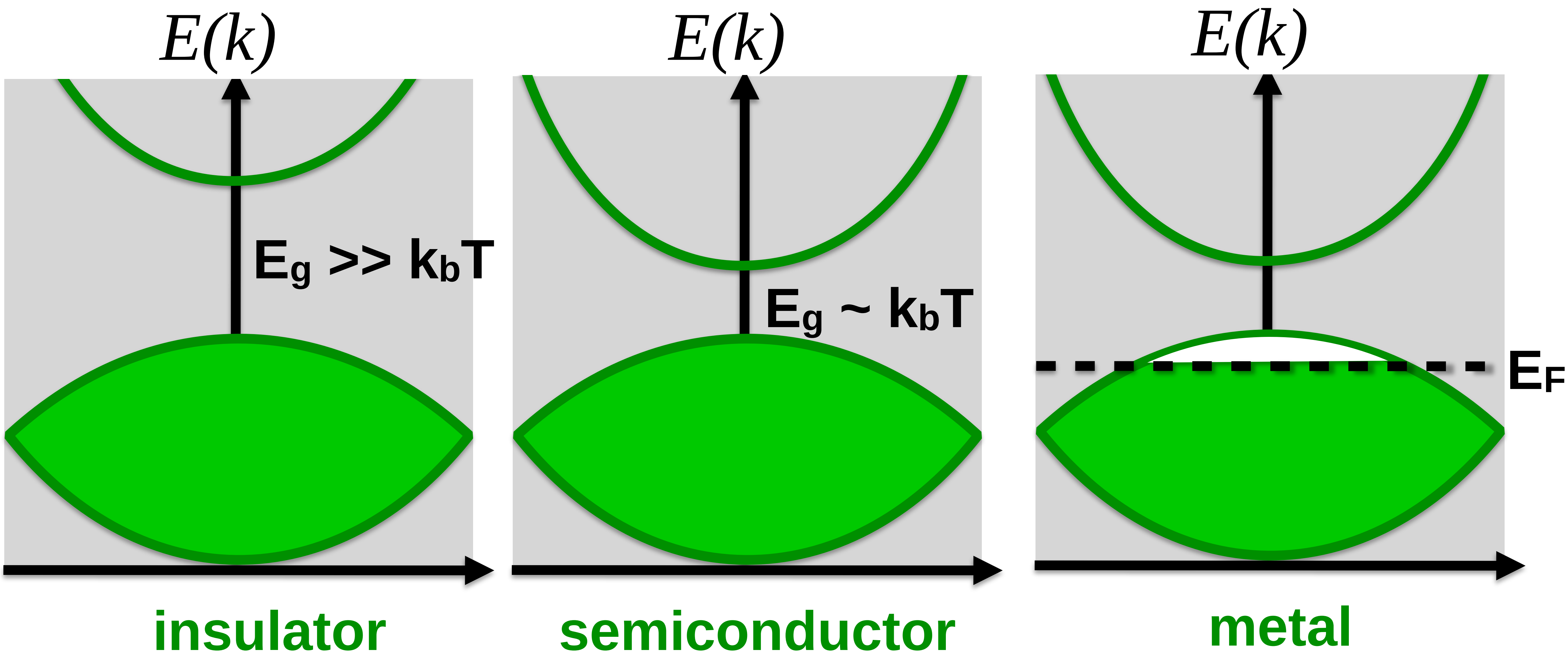
Fermi energy

Electrons can be anytime easily excited to "conduction" band



The Fermi energy marks the energy of the highest occupied state.

Questions?



The Fermi energy marks the energy of the highest occupied state.

Gallery Walk

1. Read the text for ~5 min
2. Discuss your topic with your group and together design a poster.

Your topic is printed on the cover page!

The topics are:

1. Types of Bonds
2. Covalent Bonding
3. Ionic Bonding
4. Metallic Bonding
5. Hydrogen and Dispersion Bonding
6. Distortion of Bonds

Gallery Walk

1. Mix groups – so new groups has someone from each group – explain the poster you are standing at.

2. Move on to the next poster at the signal.

Interesting information

Energy converter:
https://www.colby.edu/chemistry/PChem/Hartree.html