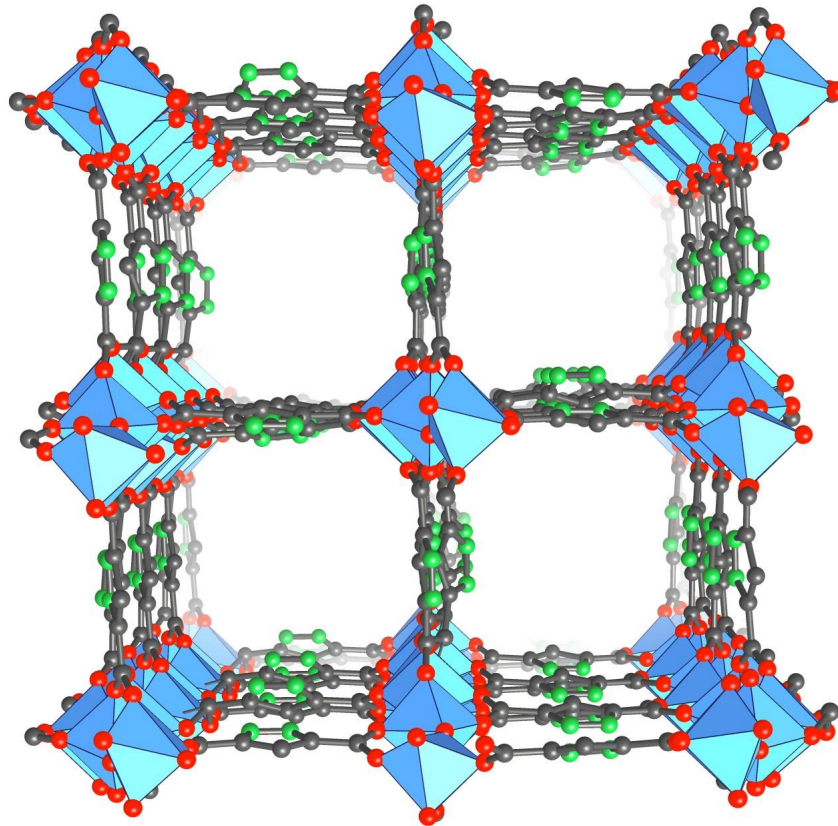


# DFT and periodic systems

*“How Chemistry and Physics Meet in the Solid State” – Roald Hoffmann, Angew Chemie 26 (1987) 846-878*

*“Iterative minimization techniques for ab initio total energy calculations: molecular dynamics and conjugate gradients” – Payne et al., Reviews of Modern Physics, 64 (1992) 1045*



June 14, 2022

What systems might we be interested in that are periodic?

?

# What systems might we be interested in that are periodic?

3D - solids

metals, metal oxides, carbon, semiconductors,

1D and 2D:

carbon nanotubes, graphene, surfaces

What properties might we want to calculate?

?

# What properties might we want to calculate?

Phase diagrams (oxidation, mixing)

Compression/expansion

Cohesive energies

Electronic properties (conductivity, excitation energies/absorption spectra)

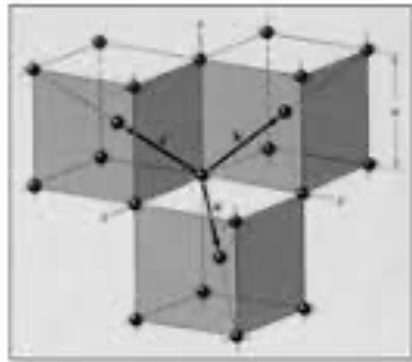
Surfaces – adsorption of molecules, reactivity

Electronic structure calculations on periodic systems (think, “solids”) will include some differences in execution

- 1) Specifying the structure of a solid requires **basis vectors** and a **basis** (ie, a “unit cell”) (familiarity?)
- 2) The number of atoms in a solid is effectively infinite – our code needs to express the periodicity of the potential (ie, an atom in a “unit cell” needs to feel those not in its “unit cell”)
- 3) Electron density is not (necessarily) near our atoms and exponentially decaying as we move away from them, as in a molecule. In a solid, atoms and electrons fill (most) space. Unclear if it is computationally most efficient to use atomic orbitals as our basis set.

1) Specifying the structure of a solid requires **basis vectors** and a **basis** (ie, a “unit cell”) → 3D

Body-centered cubic (BCC)



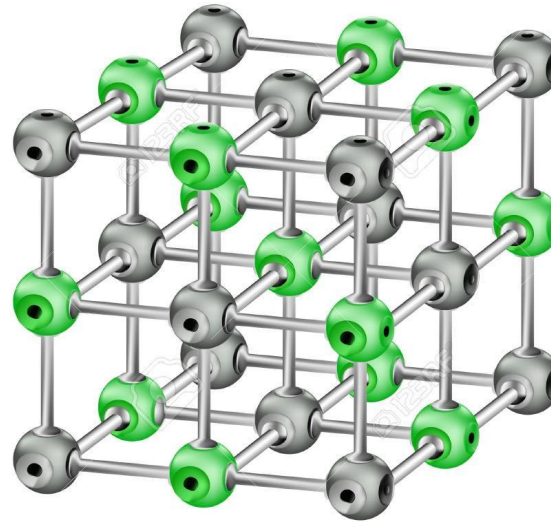
- Primitive translation vectors

$$\vec{a}' = \frac{a}{2} (\hat{x} + \hat{y} - \hat{z})$$

$$\vec{b}' = \frac{a}{2} (-\hat{x} + \hat{y} + \hat{z})$$

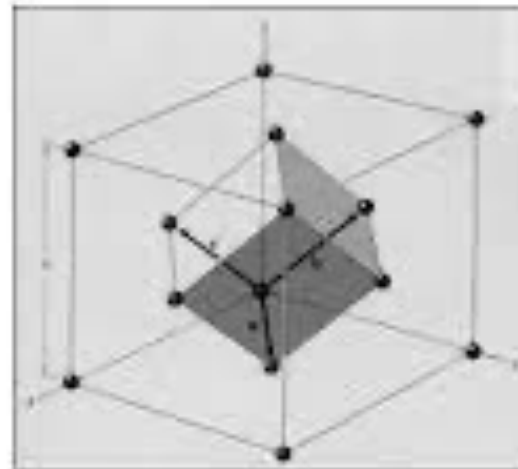
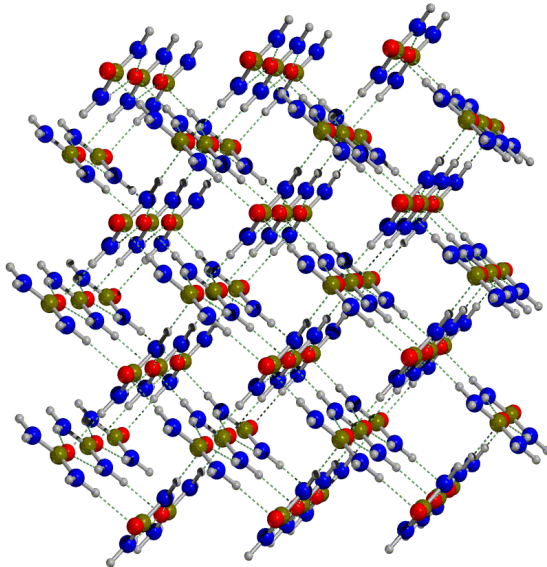
$$\vec{c}' = \frac{a}{2} (\hat{x} - \hat{y} + \hat{z})$$

orthogonal vectors of unit length



Download from  
Materials  
Project,  
OQMD,  
AFLOWLib....

Face-centered cubic (FCC)



- Primitive translation vectors

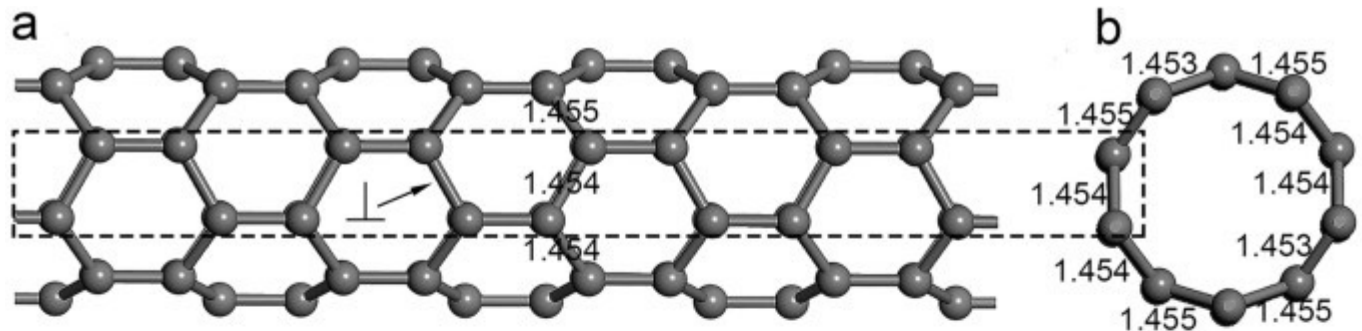
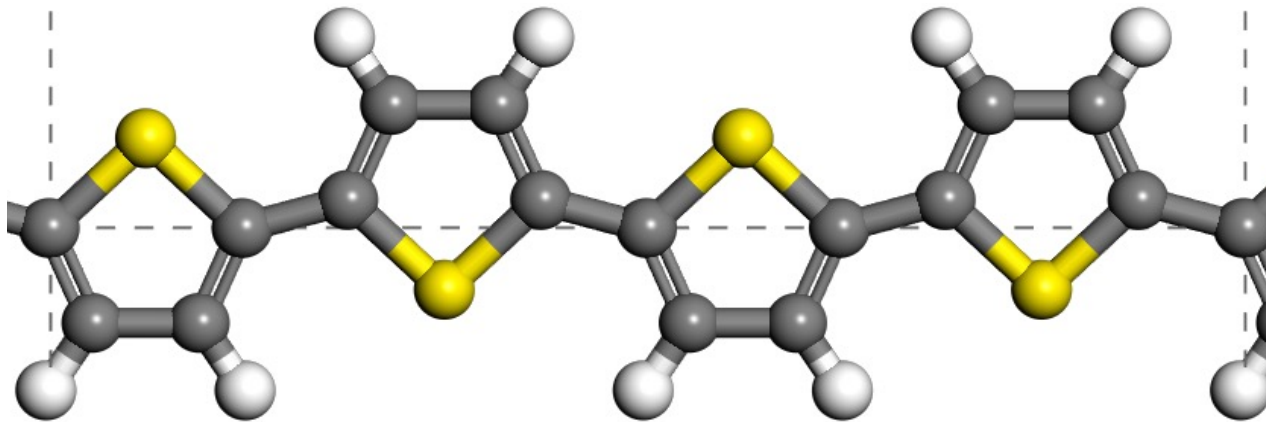
$$\vec{a}' = \frac{a}{2} (\hat{x} + \hat{y});$$

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

$$\vec{c}' = \frac{a}{2} (\hat{z} + \hat{x}).$$

# 1) Specifying the structure of a solid requires **basis vectors** and a **basis** (ie, a “unit cell”) → **1D**

For 1D – one basis vectors repeats the system, the other 2 are made large enough to avoid interaction between repeated cells (because the code is typically 3D periodic)

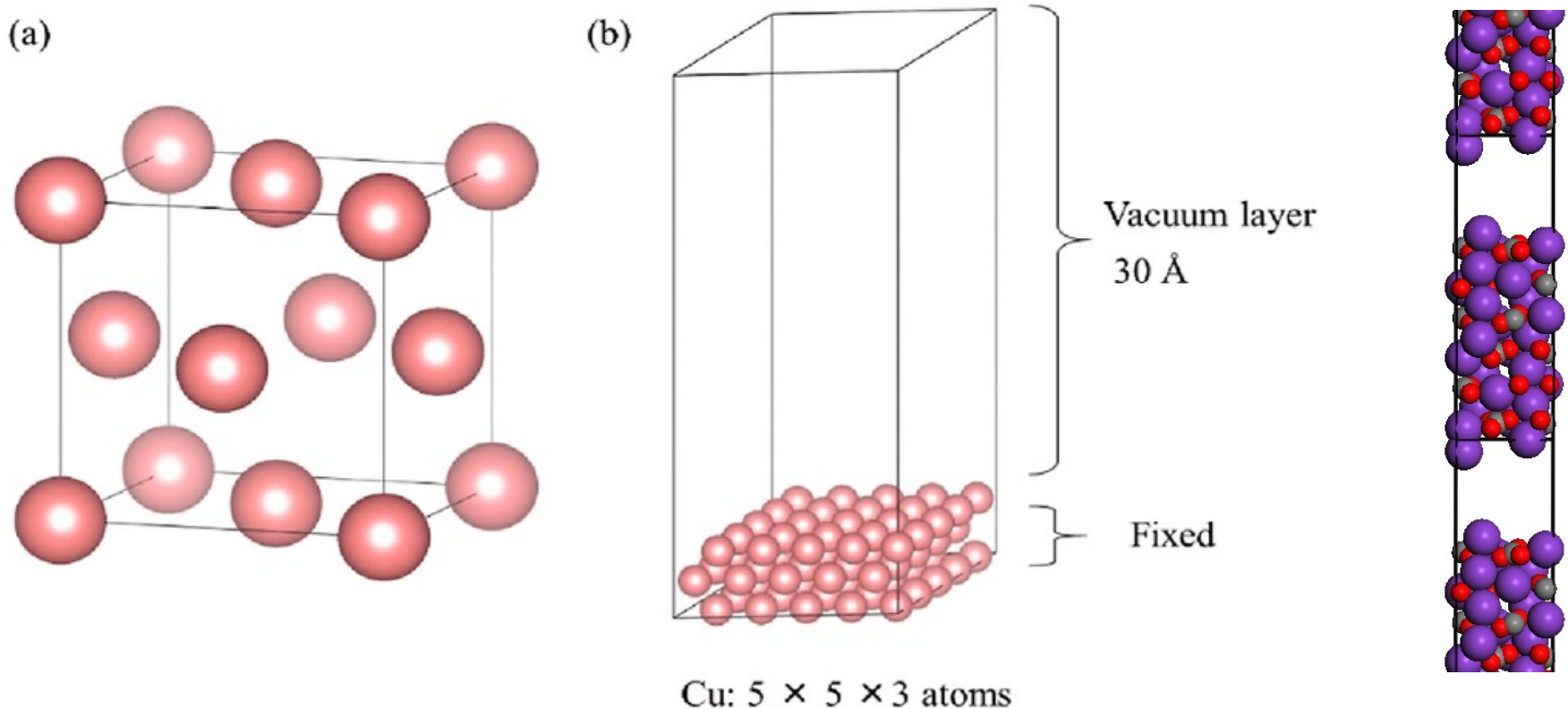


How to handle 2D?



# 1) Specifying the structure of a solid requires **basis vectors** and a **basis** (ie, a “unit cell”) → **2D**

For a surface – 2 basis vectors tell how the atoms in our surface repeat, and the third is long to avoid interaction between period cells.



Subtleties – long is long enough? Hard if surface has a big dipole moment, then interaction is long range. Codes include correction approaches....

We can add non-periodic features by making repeats long enough that whatever is not periodic doesn't interact (**0D**)

A low concentration defect (vacancy in picture, could be dopant, dislocation, etc) in a solid

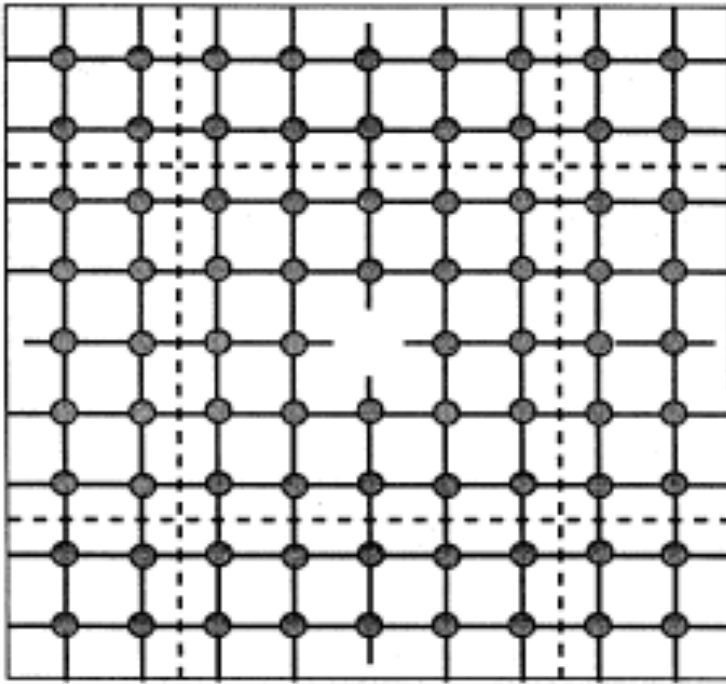
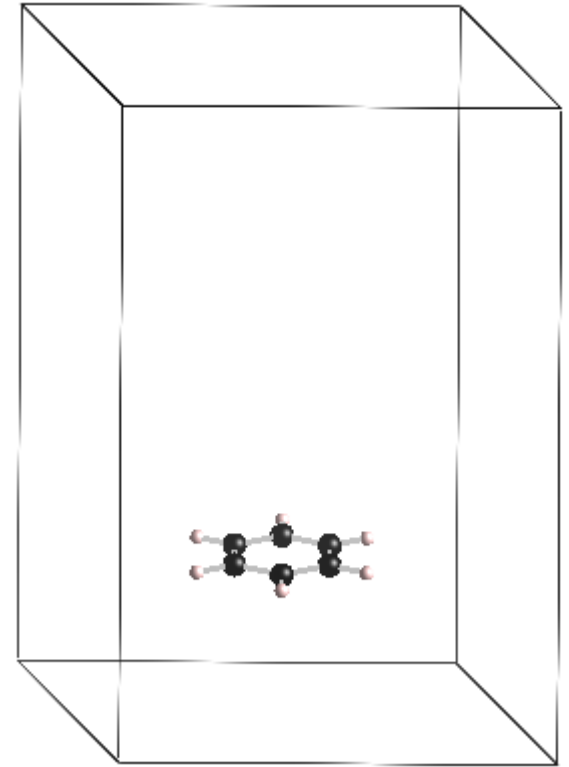


FIG. 2. Schematic illustration of a supercell geometry for a point defect (i.e., vacancy) in a bulk solid. The supercell is the area enclosed by the dashed lines.



Electronic structure calculations on periodic systems (think, “solids”) will include some differences in execution

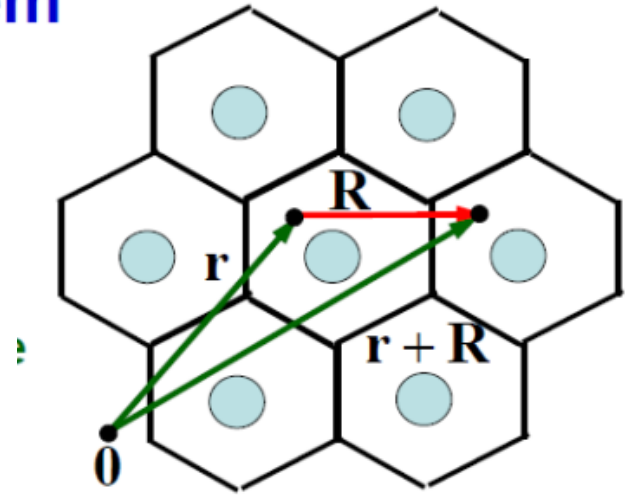
- 1) Specifying the structure of a solid requires **basis vectors** and a **basis** (ie, a “unit cell”) (familiarity?)
- 2) **The number of atoms in a solid is effectively infinite – our code needs to express the periodicity of the potential (ie, an atom in a “unit cell” needs to feel those not in its “unit cell”)**
- 3) Electron density is not (necessarily) near our atoms and exponentially decaying as we move away from them, as in a molecule. In a solid, atoms and electrons fill (most) space. Unclear if it is computationally most efficient to use atomic orbitals as our basis set.

2) The number of atoms in a solid is effectively infinite – our code needs to express the periodicity of the potential

## Bloch's theorem

Periodic potential  $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$   
(translational symmetry)

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



Ewald summation, math – can express the infinite number of interactions in periodic cells in terms unit vectors

$$E_{\text{ion}} = \frac{1}{2} \sum_{I,J} Z_I Z_J e^2 \left\{ \sum_l \frac{\text{erfc}(\eta |\mathbf{R}_1 + \mathbf{l} - \mathbf{R}_2|)}{|\mathbf{R}_1 + \mathbf{l} - \mathbf{R}_2|} - \frac{2\eta}{\sqrt{\rho}} \delta_{IJ} + \frac{4\pi}{\Omega} \sum_{\mathbf{G} \neq 0} \frac{1}{|\mathbf{G}|^2} \exp \left[ -\frac{|\mathbf{G}|^2}{4\eta^2} \right] \cos[(\mathbf{R}_1 - \mathbf{R}_2) \cdot \mathbf{G}] - \frac{\pi}{\eta^2 \Omega} \right\}, \quad (2.17)$$

Electronic structure calculations on periodic systems (think, “solids”) will include some differences in execution

- 1) Specifying the structure of a solid requires basis vectors and a basis (ie, a “unit cell”) (familiarity?)
- 2) The number of atoms in a solid is effectively infinite – our code needs to express the periodicity of the potential (ie, an atom in a “unit cell” needs to feel those not in its “unit cell”)
- 3) **Electron density is not (necessarily) near our atoms and exponentially decaying as we move away from them, as in a molecule. In a solid, atoms and electrons fill (most) space. Unclear if it is computationally most efficient to use atomic orbitals as our basis set. (And other complexities of representing a periodic electronic structure.....)**

# Bloch's Theorem – Write the wavefunction as a product of a cell periodic part and a wave-like part

## 1. Bloch's theorem

Bloch's theorem states that in a periodic solid each electronic wave function can be written as the product of a cell-periodic part and a wavelike part (see Ashcroft and Mermin, 1976),

$$\psi_i(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] f_i(\mathbf{r}) . \quad (2.7)$$

The cell-periodic part of the wave function can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$f_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}] , \quad (2.8)$$

where the reciprocal lattice vectors  $\mathbf{G}$  are defined by  $\mathbf{G} \cdot \mathbf{l} = 2\pi m$  for all  $\mathbf{l}$  where  $\mathbf{l}$  is a lattice vector of the crystal and  $m$  is an integer. Therefore each electronic wave function can be written as a sum of plane waves,

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] . \quad (2.9)$$

*$f_i(\mathbf{r})$  is effectively what we did yesterday – a wavefunction around the atoms in our system (now, in our “unit cell”)*

*2.8 – come back to this, but says we can use “plane waves” rather than atomic orbitals for  $f$*

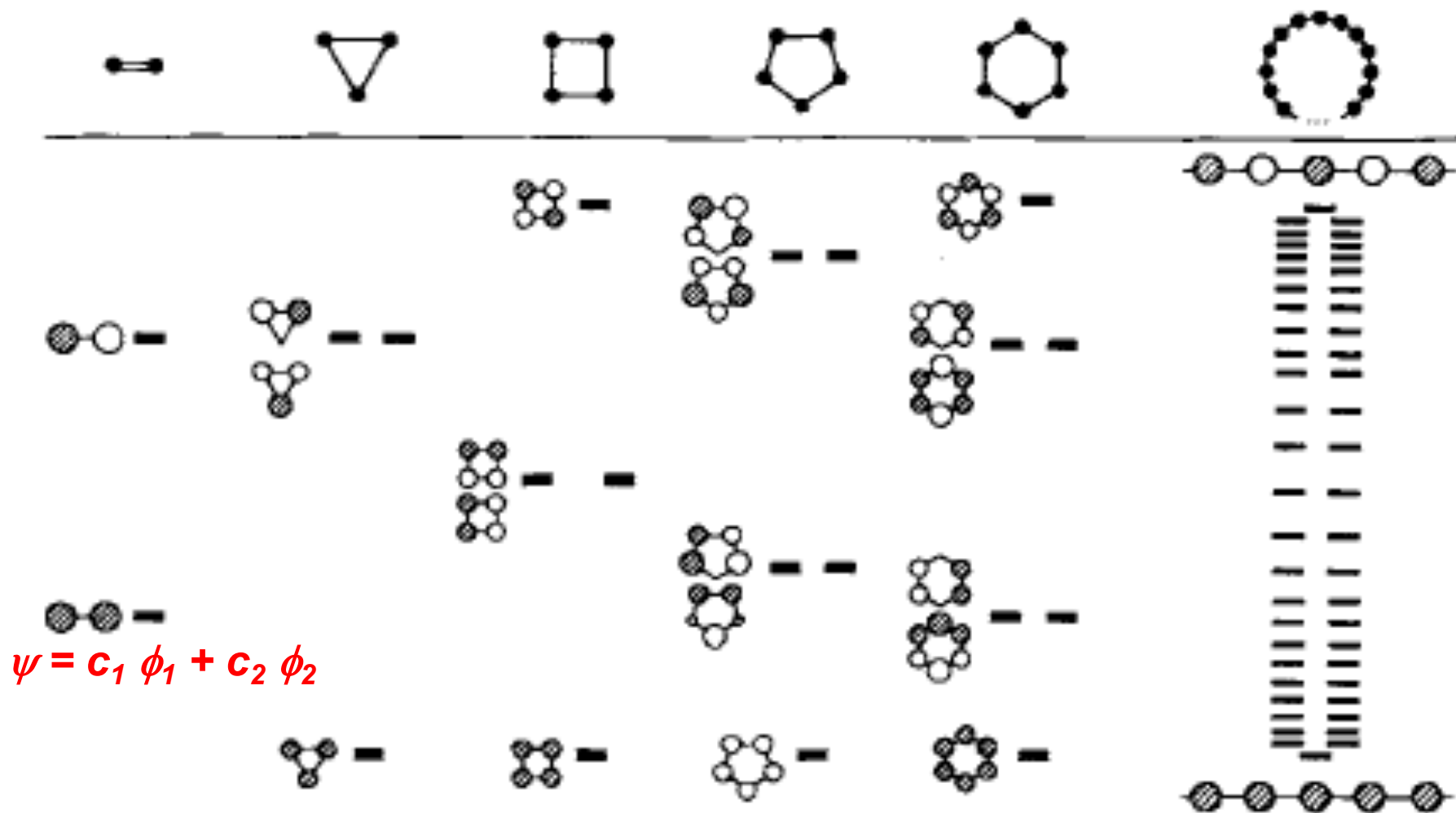
*The Hoffmann paper helps us understand the “cell-periodic part”*

Familiarity with “band structure” of a solid?

?

In solids, the “repeated bonding” of many atoms to each other produces bands of states (orbitals) differing slightly in energy

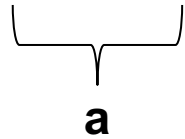
*“How Chemistry and Physics Meet in the Solid State” – Roald Hoffmann, Angew Chemie 26 (1987) 846-878*



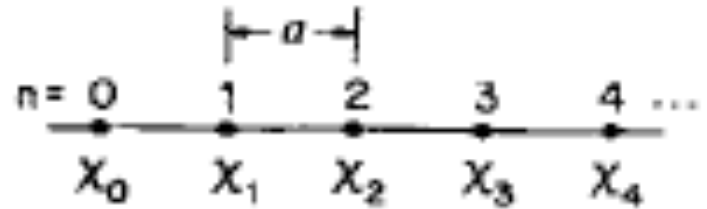
*The circle is  $f_i(r)$  – a  $s$  orbital centered on an atom (ie,  $\phi_i \rightarrow$  today we will use  $\chi$  to steal from Hoffmann paper)*



A 1-dimensional H-chain helps us think about how we might mathematically express these states



$\searrow$   
 $\chi_n = 1s \text{ Orbital}$



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

*When you see  $e^{iy}$ , think  $\sin(y)$*

$k=0 \quad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$

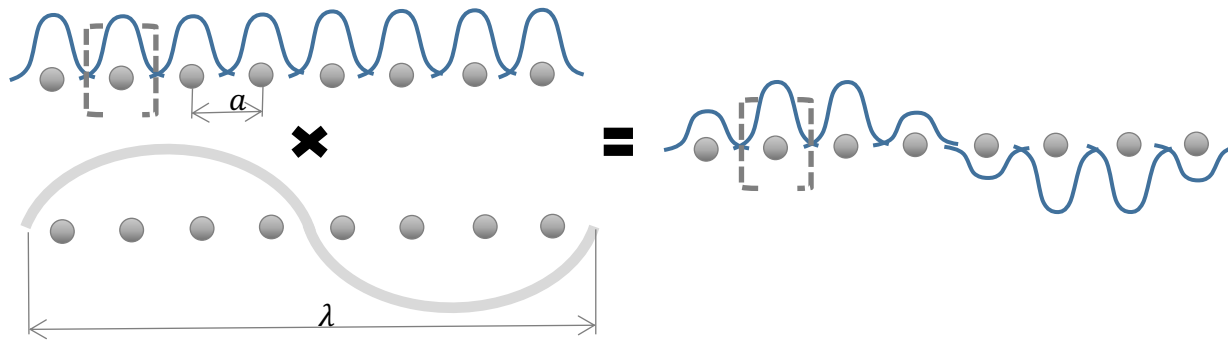
A horizontal line with four shaded circles representing the spatial distribution of the  $k=0$  state, where all sites have the same amplitude.

$k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$

A horizontal line with four circles representing the spatial distribution of the  $k=\pi/a$  state. The circles alternate between shaded and unshaded, representing a wave with a period of two lattice sites.

Note  $e^0 = 1$  and therefore  $k=0$  just gives a constant 1  
 $e^{i\pi n} = -1^n$

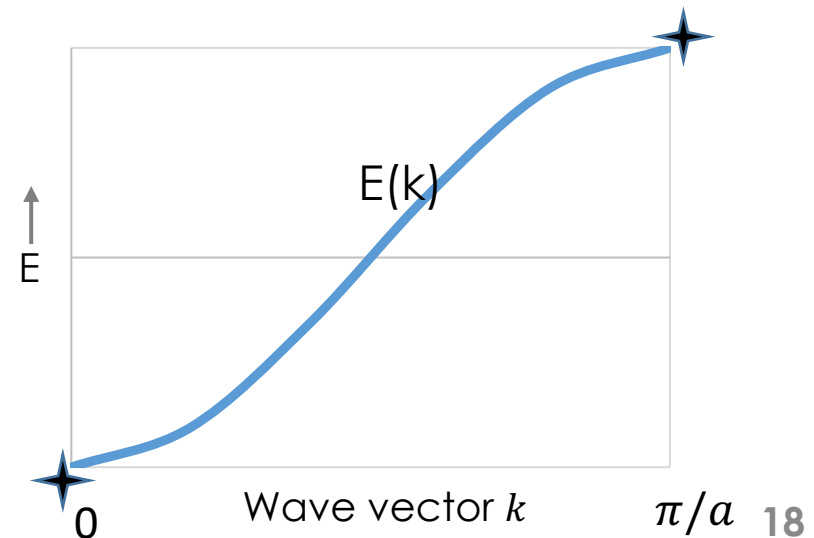
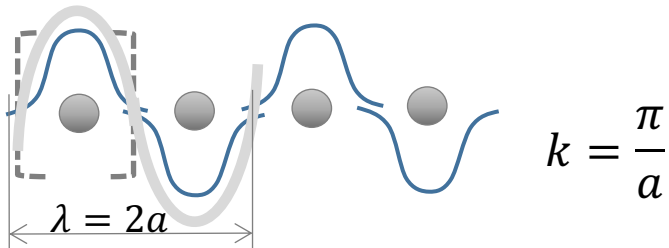
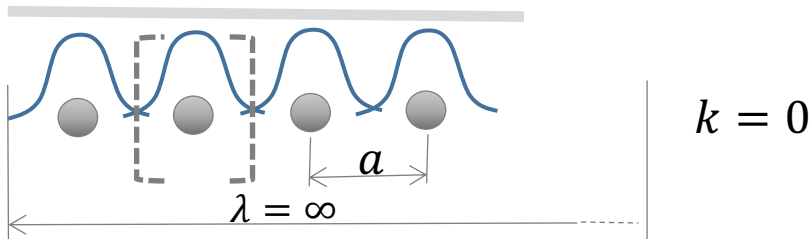
# What the orbitals look like at different $k$ , and the “band structure” this leads to.....



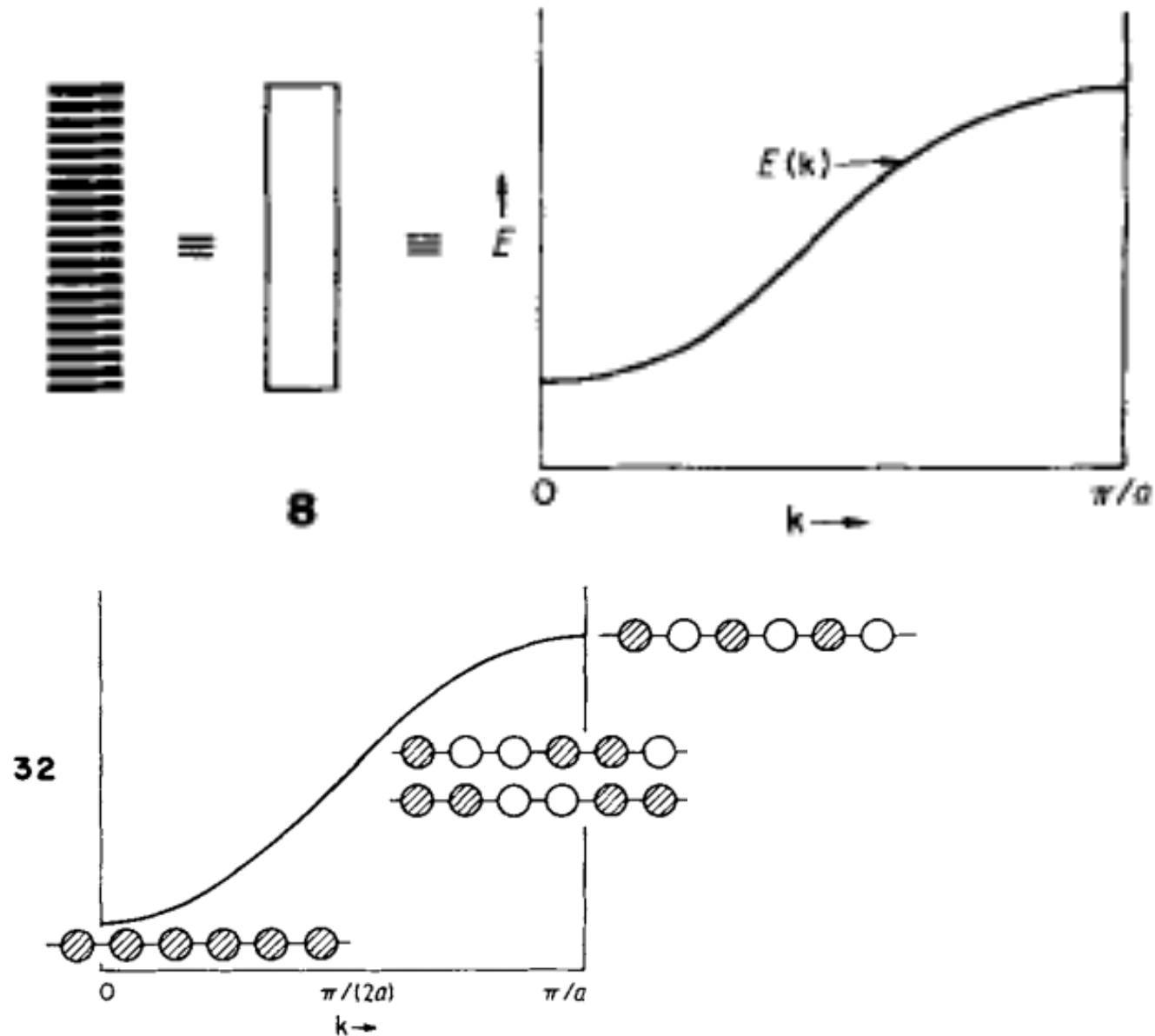
$$\Psi = e^{ikx} \underbrace{f(x)}_{\text{Periodic function}}$$

Plane wave  $\sim \cos(kx)$   
 Wave vector  $\rightarrow k = \frac{2\pi}{\lambda}$

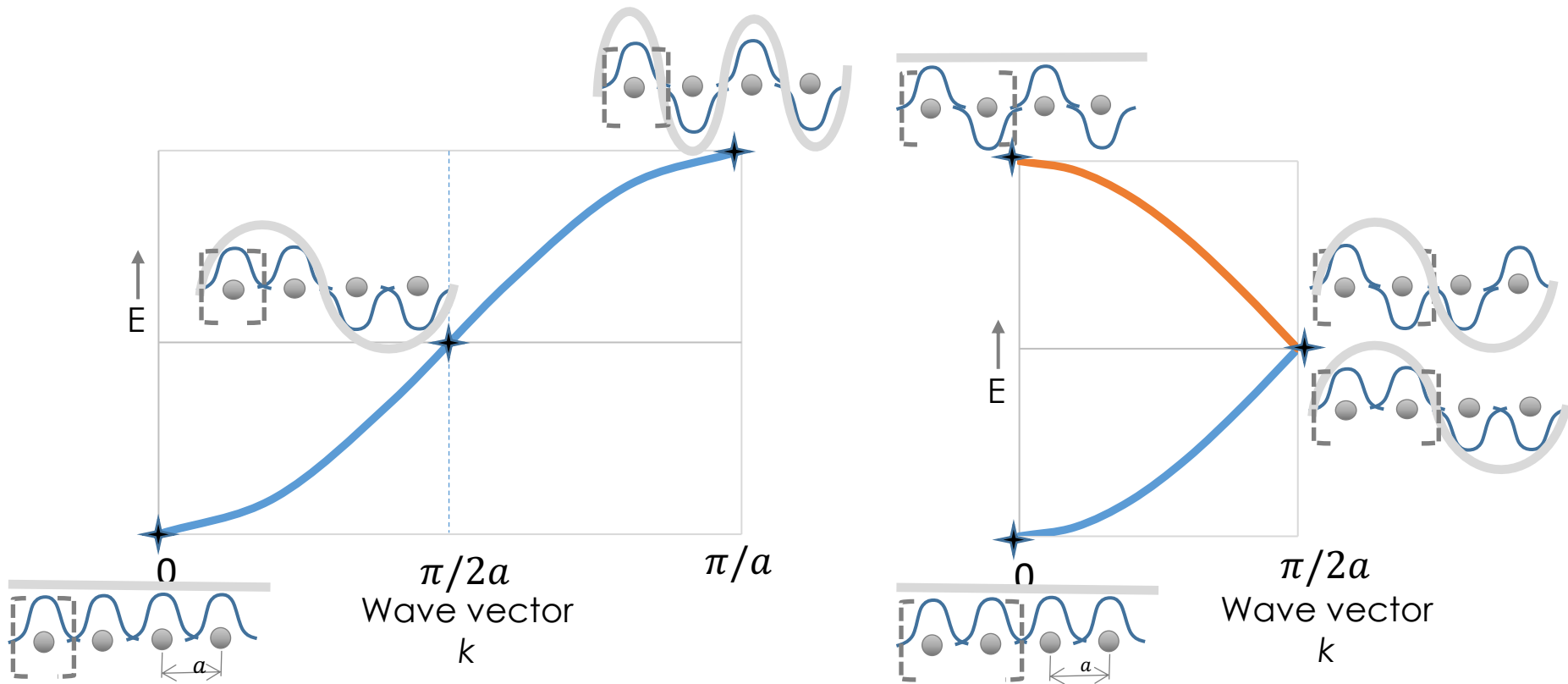
$$P = |\Psi^2|$$



A “band” is then a number of states close together in energy that differ in “k”



# Bands fold upon doubling the unit cell



“See how they run” – the variation of energy with  $k$  tells us something about the orbital character, band identify

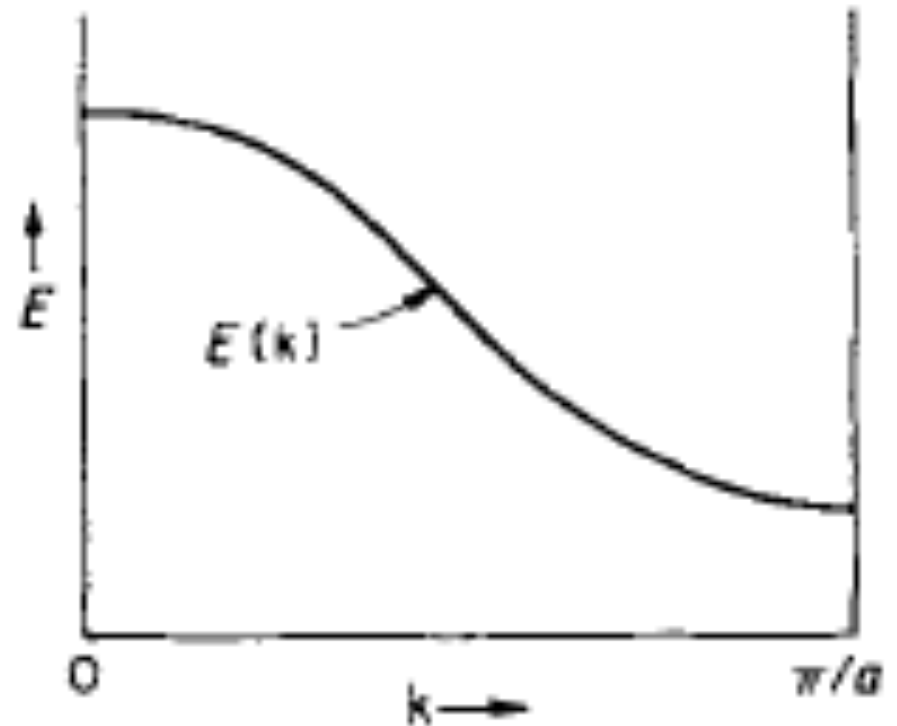
$$\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



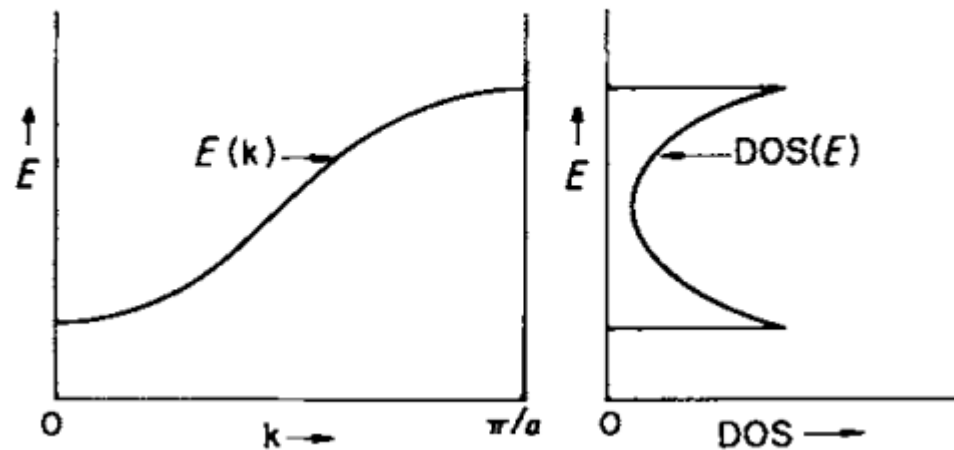
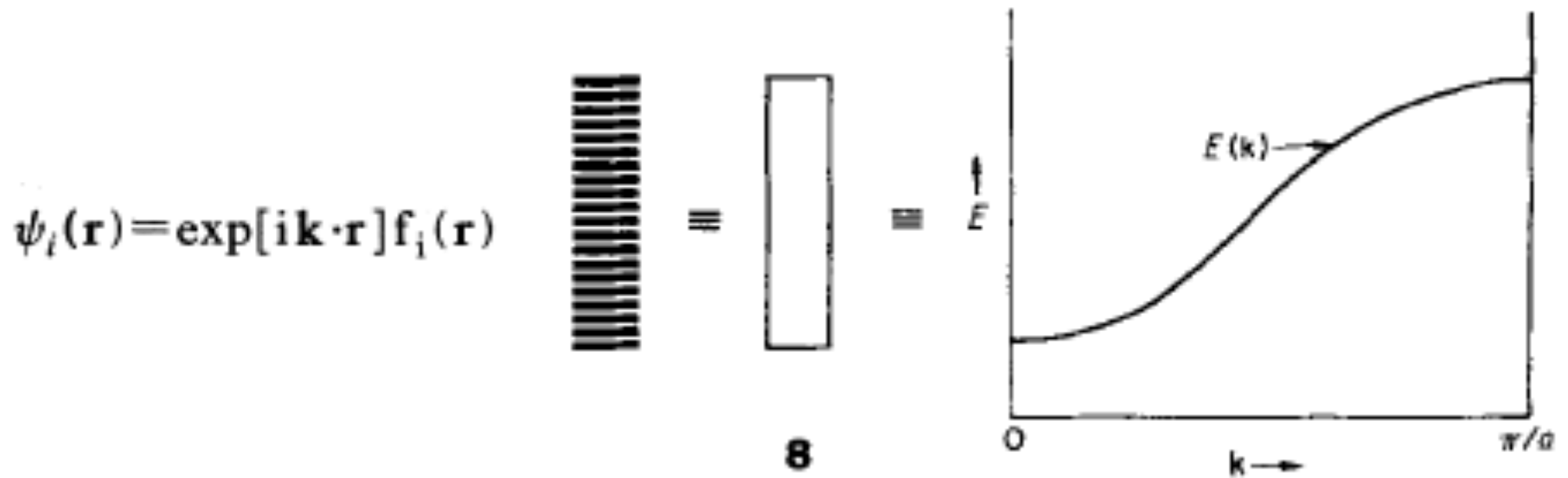
$$\psi_{\frac{\pi}{a}} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$



9

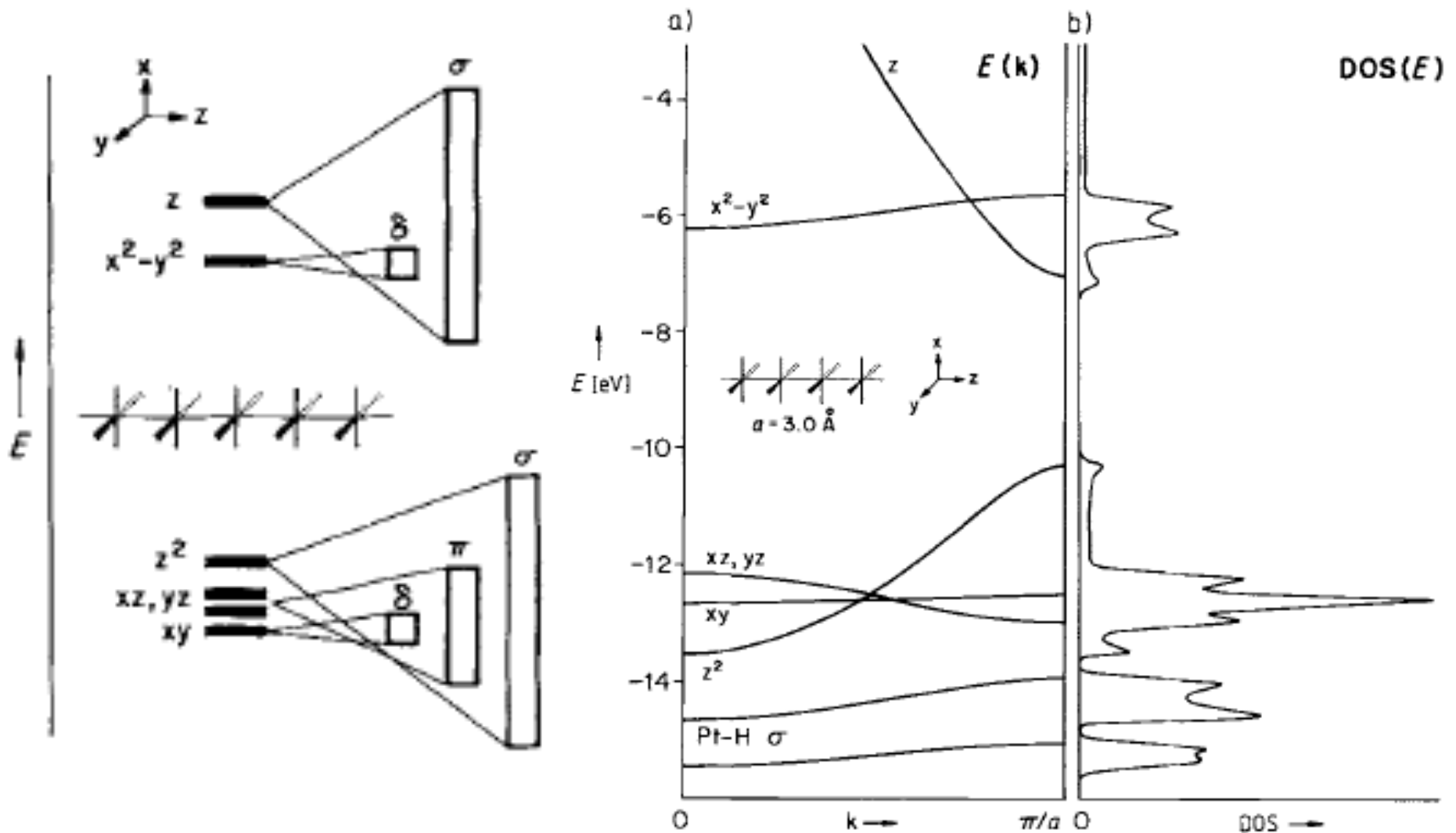


A “density of states” plot shows us how many orbitals we have at each energy



$\text{DOS}(E) dE = \text{number of levels between } E \text{ and } E + dE$

Orbital diagram becomes a “Density of states” plot



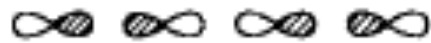
*but back to periodic DFT calculations (Payne et al.).....*

# K Point Sampling – energy will converge as more k-points included

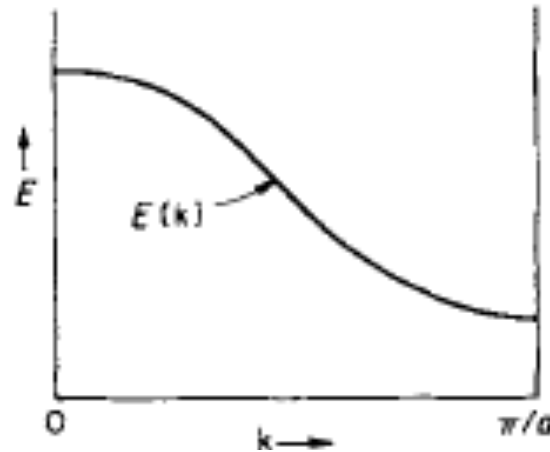
$$\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



$$\psi_{\frac{\pi}{a}} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$

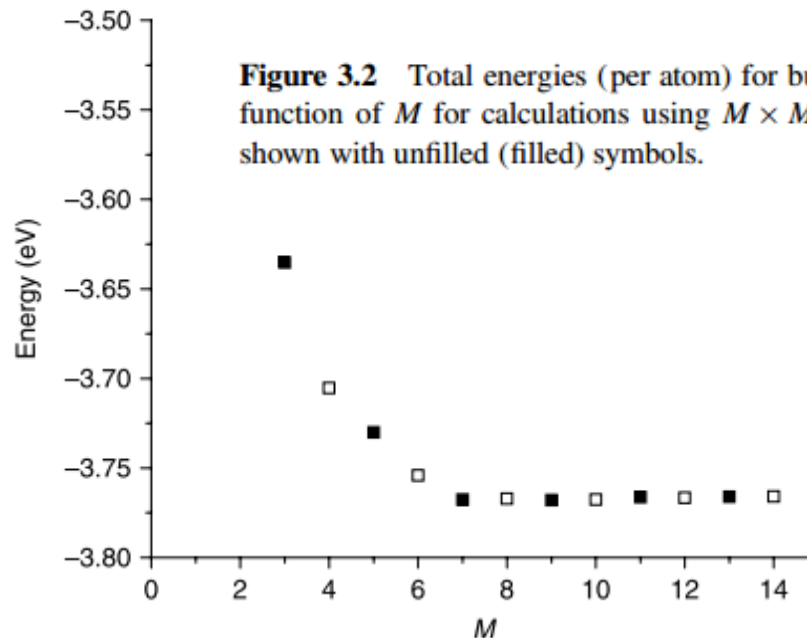


9



$$\psi_i(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] f_i(\mathbf{r})$$

$$f_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}]$$

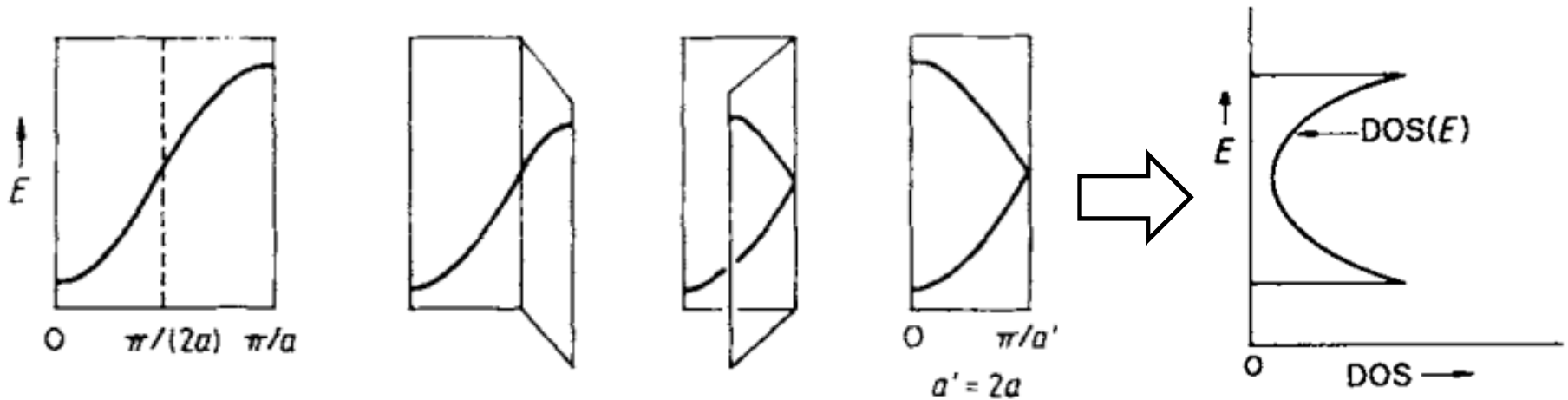
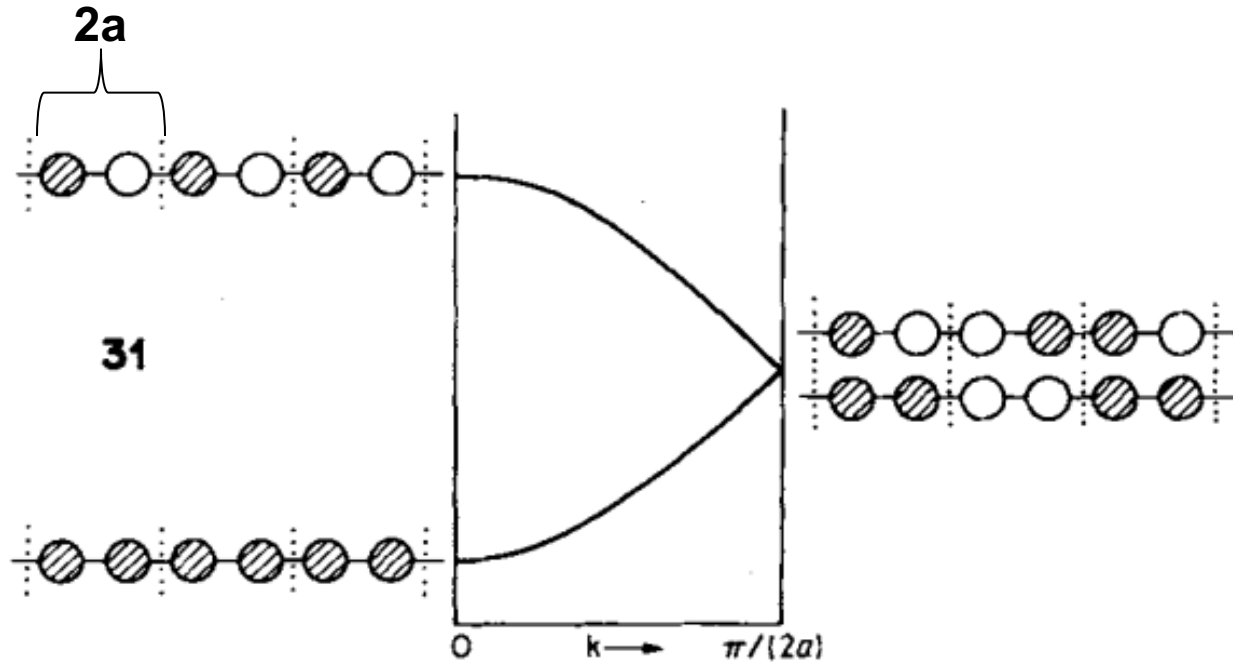


**Figure 3.2** Total energies (per atom) for bulk Cu calculated as described in Table 3.2 as a function of  $M$  for calculations using  $M \times M \times M$   $k$  points. Results with even (odd)  $M$  are shown with unfilled (filled) symbols.

Not always monotonic  
like this graph



A bigger cell (longer basis vector) means we need less k-points to converge our k-point sampling



# Bloch's Theorem – Write the wavefunction as a product of a cell periodic part and a wave-like part

## 1. Bloch's theorem

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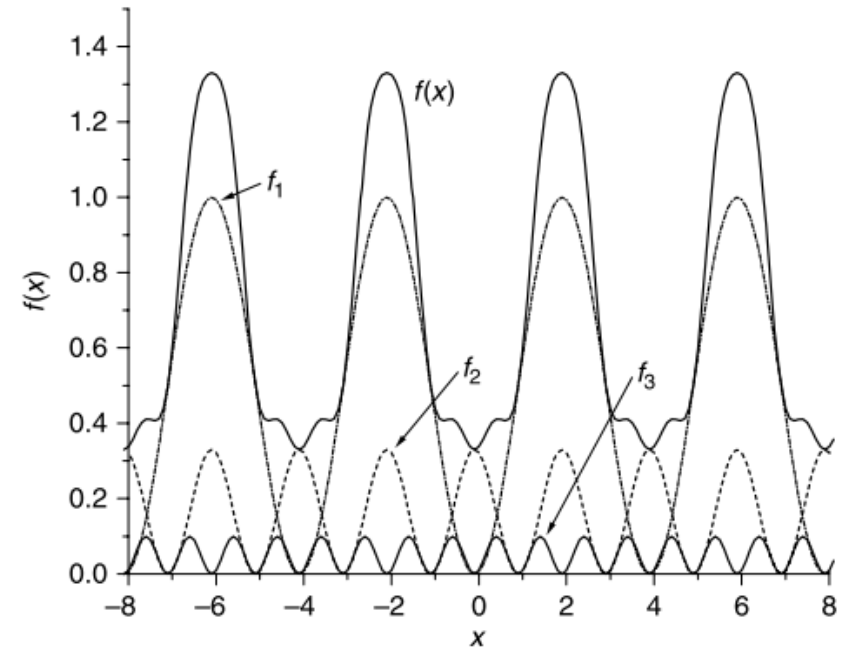
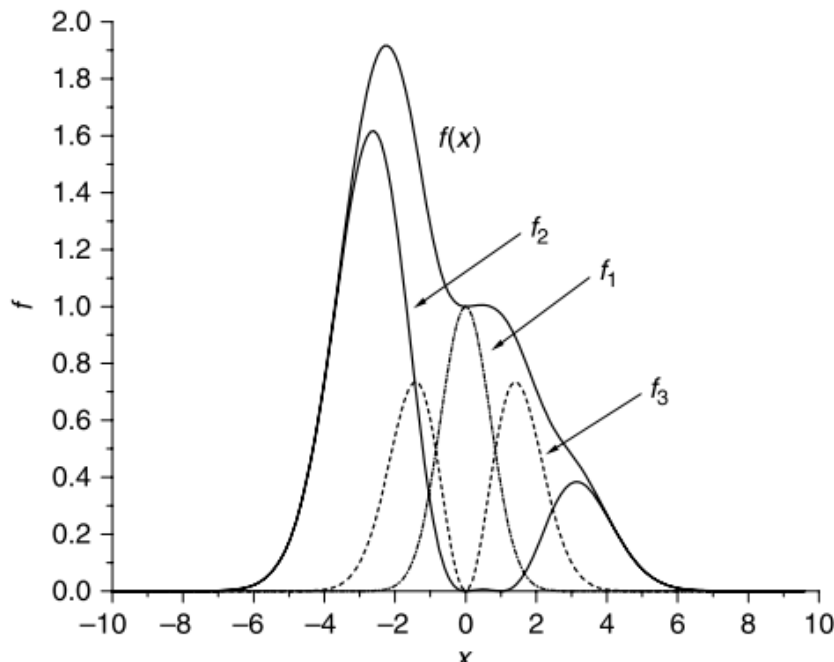
*$f_i(\mathbf{r})$  is effectively what we did yesterday – a wavefunction around the atoms in our system (now, in our “unit cell”)*

*2.8 – come back to this, but says we can use “plane waves” rather than atomic orbitals for  $f$*

*The Hoffmann paper helps us understand the “cell-periodic part”*

Rather than localized (atomic orbital) basis sets, we can use plane waves (ie, “Fourier series”) for  $\psi$

$$F(x) = c_1 f_1(x) + c_2 f_2(x) + c_3 f_3(x) \\ = \sum_i c_i f_i$$



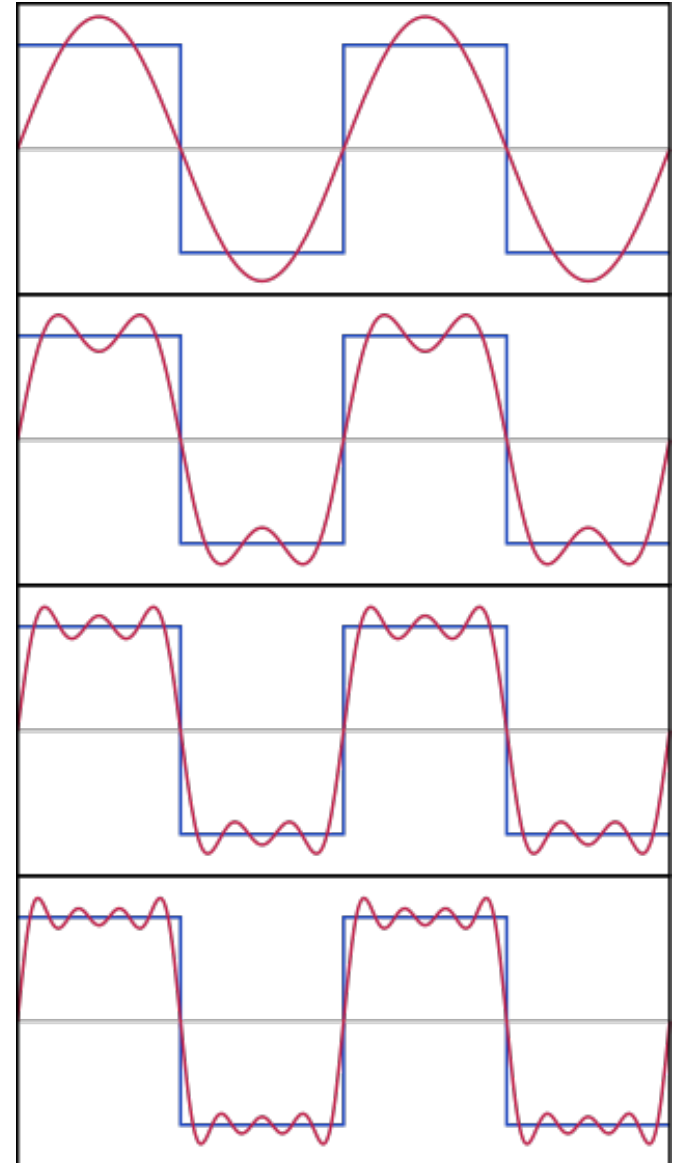
$$f_1(x) = \sin^2\left(\frac{\pi x}{4}\right),$$

$$f_2(x) = \frac{1}{3} \cos^2\left(\frac{\pi x}{2}\right),$$

$$f_3(x) = \frac{1}{10} \sin^2(\pi x).$$

# Fourier Series and Plane Waves used to represent $\psi$

$$\begin{aligned}\psi_N(x) &= \frac{a_0}{2} + \sum_{n=1}^N \left( \underbrace{A_n \sin(\phi_n)}_{a_n} \cos\left(\frac{2\pi n x}{P}\right) + \underbrace{A_n \cos(\phi_n)}_{b_n} \sin\left(\frac{2\pi n x}{P}\right) \right) \\ &= \sum_{n=-N}^N c_n \cdot e^{i \frac{2\pi n x}{P}},\end{aligned}$$



# Periodic density functional theory: plane-wave basis sets and k-point sampling

$$\psi_i(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] f_i(\mathbf{r}) \quad f_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}] \quad \psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}]$$

Bloch theorem: at each k-point, the wave function can be written as an infinite set of “plane-waves.” (If “plane-waves” bothers you – think “sine waves,” ie, expanded in a Fourier series).

The problem then reduces to solving for the coefficients in the “Fourier series” that makes up the wave function.

We can not use an infinite series, but may truncate the series at some “energy,” then try a higher energy and stop when it makes no difference. This is simpler to determine “basis set convergence” than “linear combination of atomic orbitals.” (“plane-wave basis set cut-off energy”)

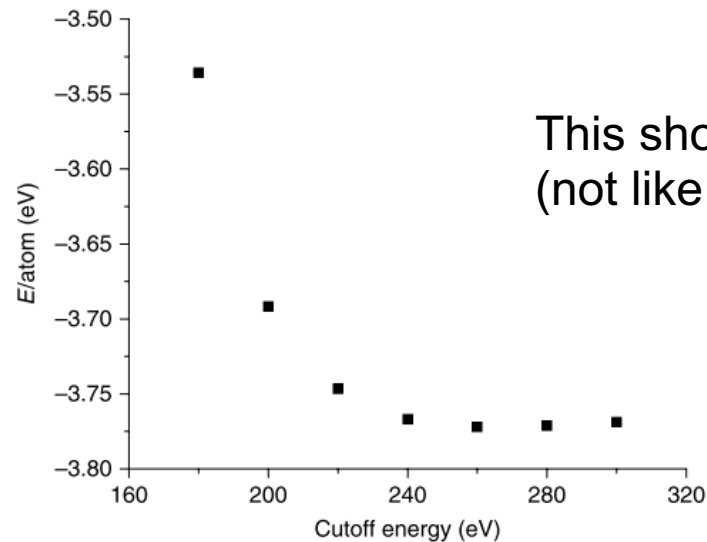
We need to solve the problem repeatedly for various “k-points” – the set of optimal wave-functions will include wave-functions at various k-points. Various methods exist to identify “special k-points” based on the cell shape.

# Energy Cutoff – Basis Set Size

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G})\mathbf{r}].$$

$$\frac{-\hbar^2}{2m} \nabla^2 \phi = E \phi \quad \longrightarrow \quad E = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2$$

$$E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2, \quad \phi_{\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| < G_{\text{cut}}} c_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G})\mathbf{r}].$$



This should always be monotonic (not like k-points). Why?

**Figure 3.4** Energy per atom of fcc Cu with a lattice constant of 3.64 Å using  $12 \times 12 \times 12$   $k$  points as a function of the energy cutoff, plotted using a similar energy scale to Fig. 3.2.

Kohn-Sham equations reduce to a “secular equation” solved with matrix diagonalization

4. Plane-wave representation of Kohn-Sham equations

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}]$$

When plane waves are used as a basis set for the electronic wave functions, the Kohn-Sham equations assume a particularly simple form. Substitution of Eq. (2.9) into (2.3) and integration over  $\mathbf{r}$  gives the secular equation

$$\sum_{\mathbf{G}'} \left[ \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{\text{ion}}(\mathbf{G} - \mathbf{G}') + V_H(\mathbf{G} - \mathbf{G}') + V_{XC}(\mathbf{G} - \mathbf{G}') \right] c_{i,\mathbf{k}+\mathbf{G}'} = \epsilon_i c_{i,\mathbf{k}+\mathbf{G}} \quad (2.10)$$

In this form, the kinetic energy is diagonal, and the various potentials are described in terms of their Fourier transforms. Solution of Eq. (2.10) proceeds by diagonalization of a Hamiltonian matrix whose matrix elements  $H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}$  are given by the terms in the brackets above. The size of the matrix is determined by the choice of cutoff energy  $(\hbar^2/2m)|\mathbf{k} + \mathbf{G}_c|^2$ , and will be intractably large for systems that contain both valence and core electrons. This is a severe problem, but it can be overcome by use of the pseudopotential approximation, as discussed in Sec. II.D.

Flow diagram for calculating the electron density at one set of nuclei positions

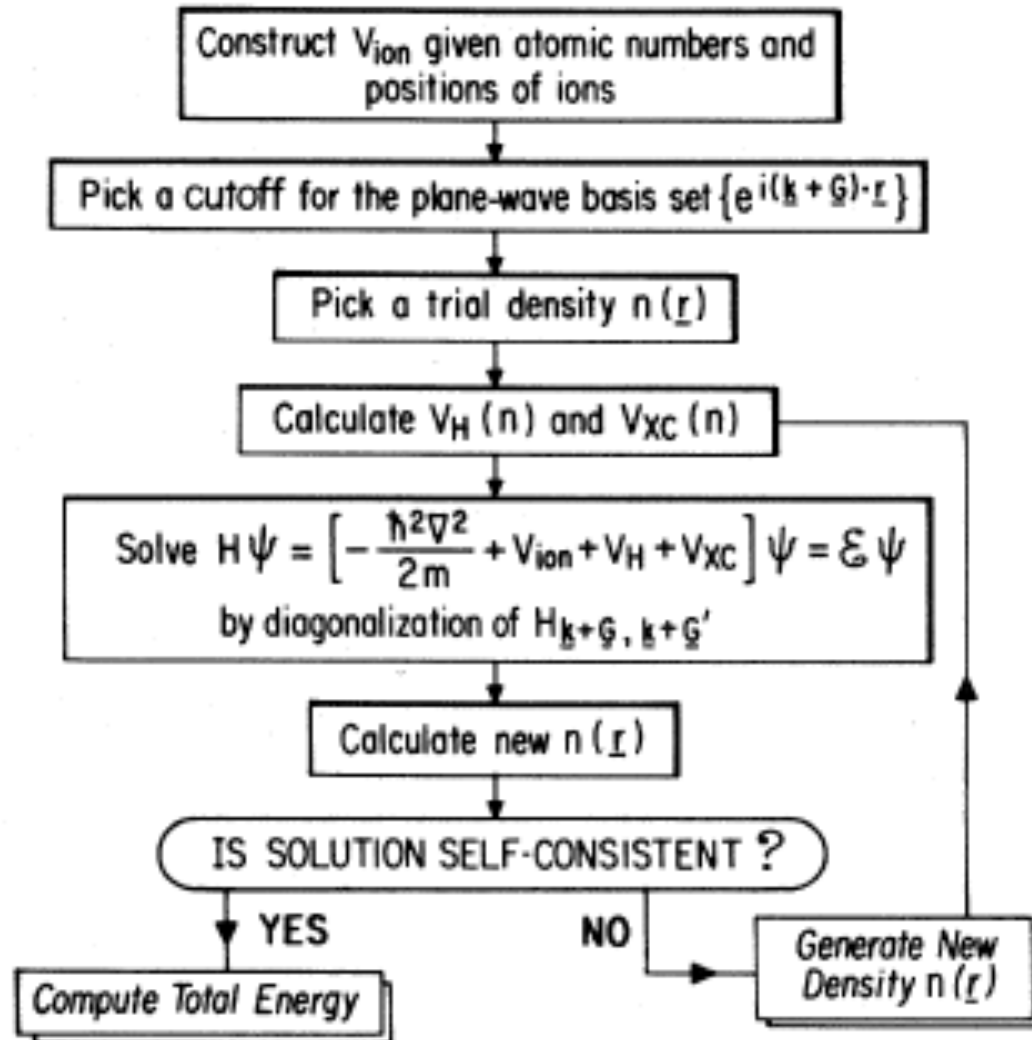


FIG. 7. Flow chart describing the computational procedure for the calculation of the total energy of a solid, using conventional matrix diagonalization.



# Flow diagram for calculating the electron density at one set of nuclei positions

*Not converged  
Pick new nuclei  
positions and  
repeat*

*Check atom forces*

*Converged*

Report  
optimized  
energy

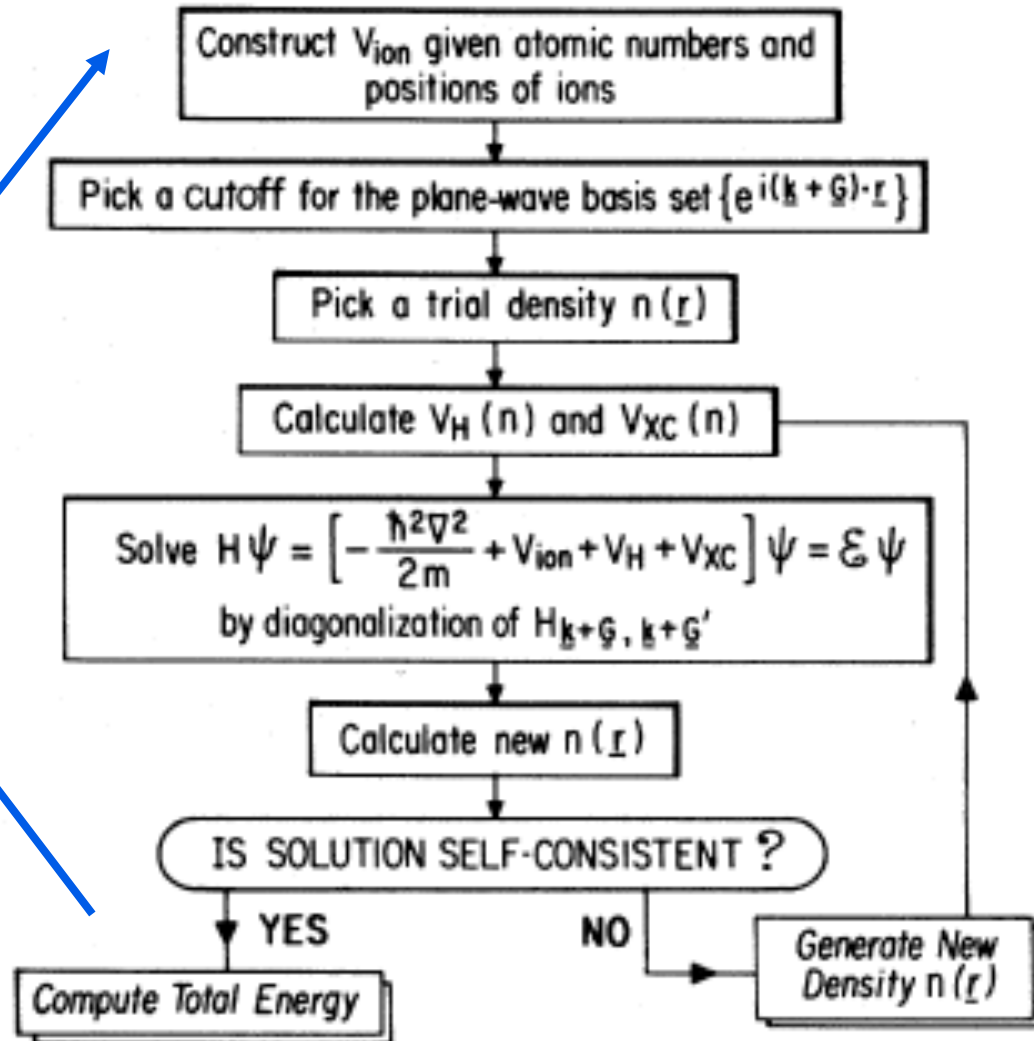


FIG. 7. Flow chart describing the computational procedure for the calculation of the total energy of a solid, using conventional matrix diagonalization.

What to optimize for a solid? Lattice constant.....

Hands-on session to optimize (manually) lattice constant of a solid

