

CHEM6085: Density Functional Theory

Lecture 11

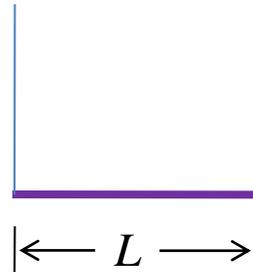
DFT for periodic crystalline solids

C.-K. Skylaris

Electron in a one-dimensional periodic box (in atomic units)

Schrödinger equation

$$-\frac{1}{2} \frac{d^2}{dx^2} \psi_n(x) = \varepsilon_n \psi_n(x)$$



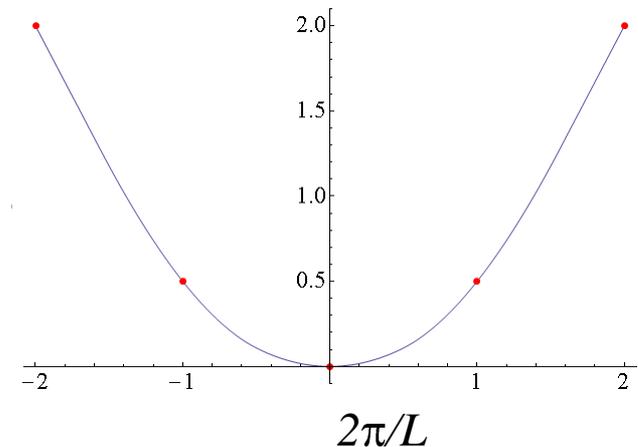
Energy eigenvalues

$$\varepsilon_n = \frac{g_n^2}{2} = \frac{2\pi^2 n^2}{L^2}$$

Eigenfunctions: plane waves

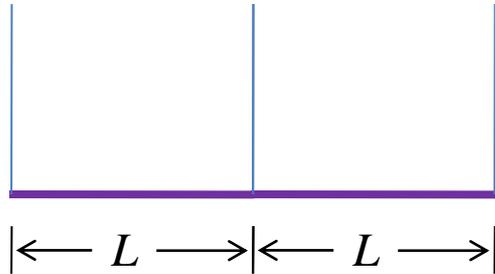
$$\psi_n(x) = \frac{1}{\sqrt{L}} e^{ig_n x} = \frac{1}{\sqrt{L}} [\cos(g_n x) + i \sin(g_n x)]$$

$$n = 0, \pm 1, \pm 2, \pm 3, \dots \quad g_n = \frac{2\pi n}{L}$$

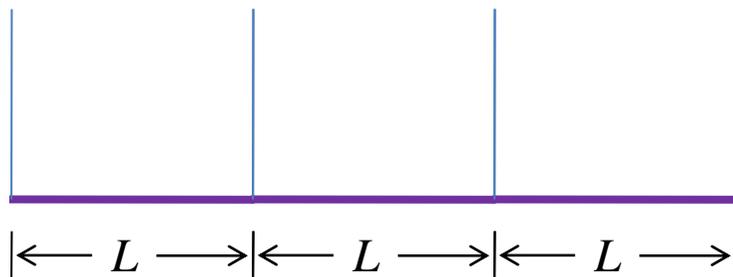
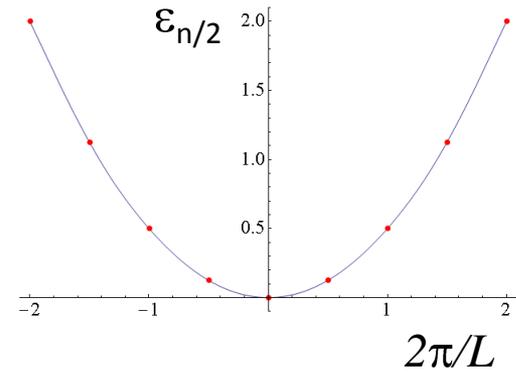


More periodic boxes

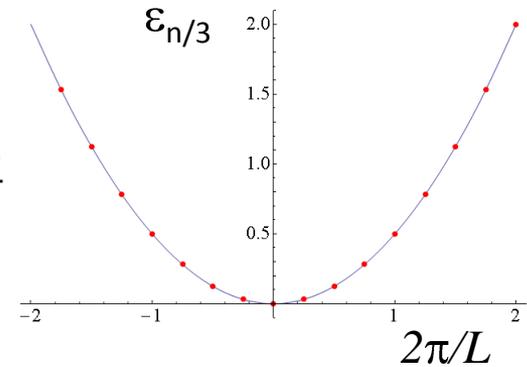
$$n = 0, \pm 1, \pm 2, \pm 3, \dots \quad \varepsilon_n = \frac{g_n^2}{2}$$



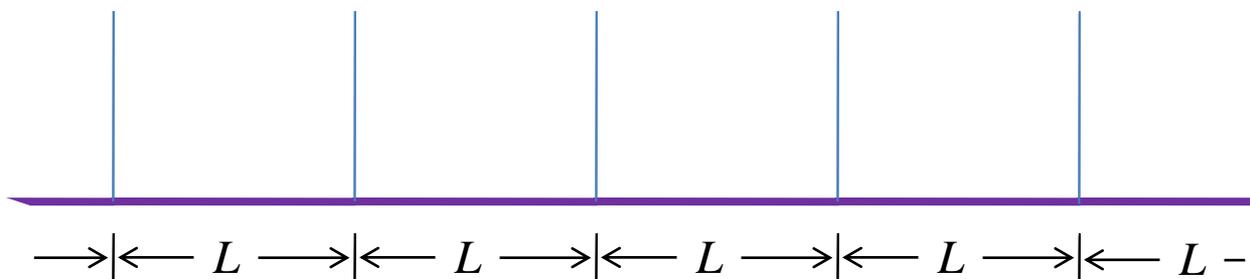
$$g_n = \frac{2\pi n}{2L}$$



$$g_n = \frac{2\pi n}{3L}$$

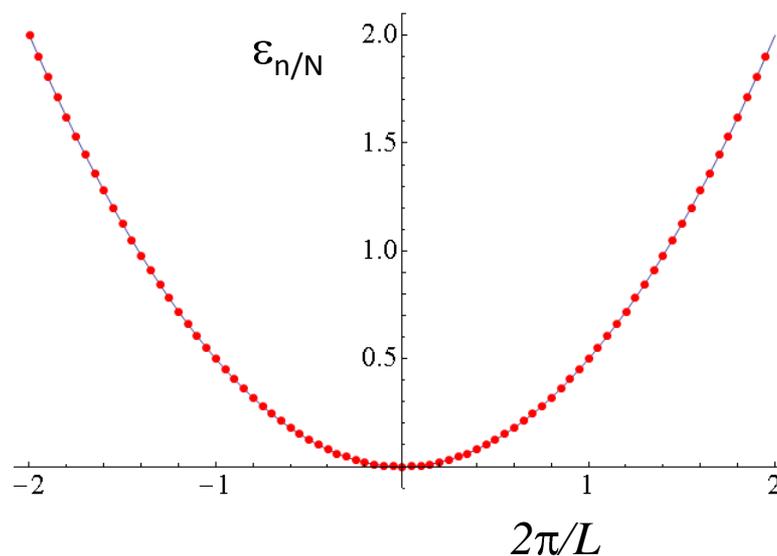


Lots and lots of periodic boxes



As the number (N) of periodic boxes increases the spacing between energy levels decreases until they form a continuum

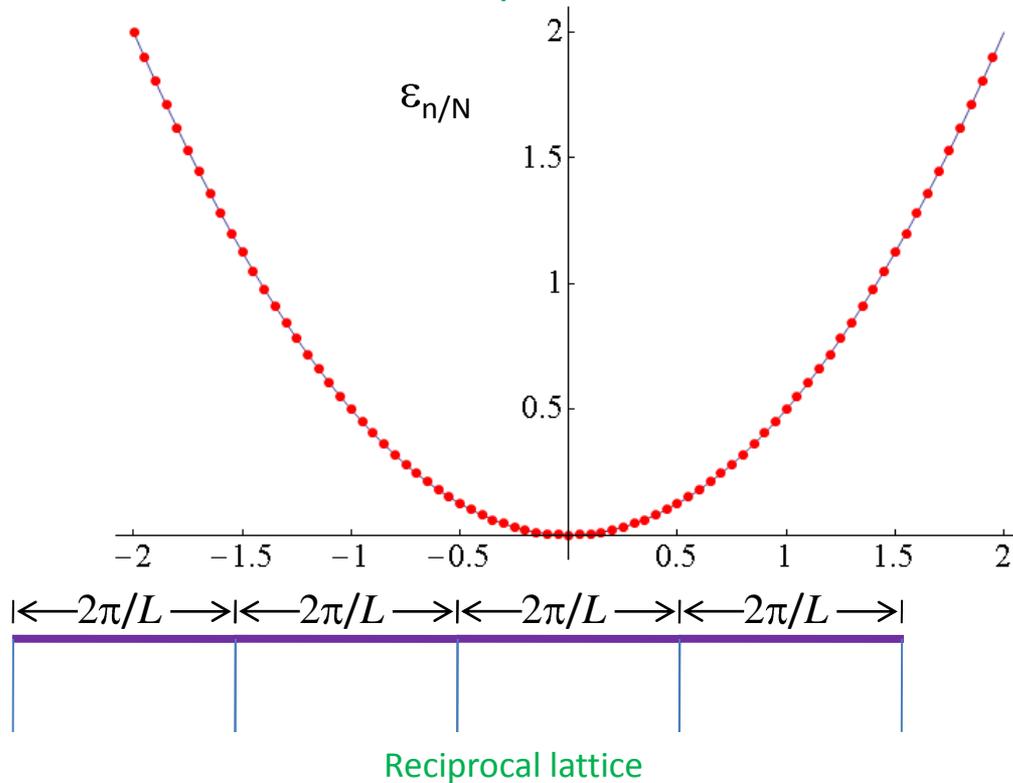
$$g_n = \frac{2\pi n}{NL}$$



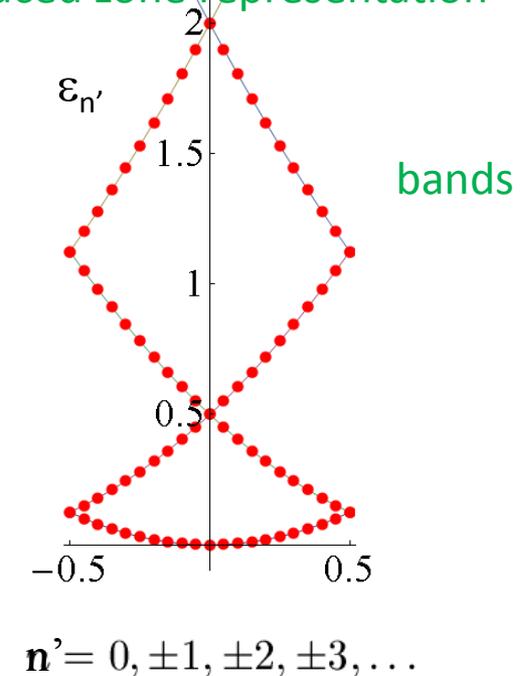
The reciprocal lattice of the independent electron

- We can treat the wavenumber g_n as a “position” in a lattice which we call the “reciprocal lattice”
- The length of the unit cell in the reciprocal lattice is $2\pi/L$

Extended zone representation



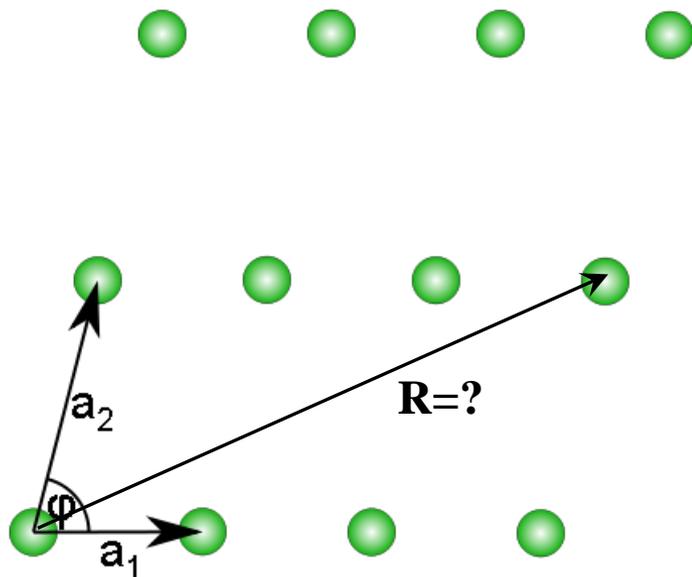
Reduced zone representation



Perfect periodic crystals: Bravais lattice (in 2D)

- An infinite lattice of points periodically repeated in space
- Each point is positioned at a lattice vector \mathbf{R}
- Any lattice vector is generated as a linear combination of the primitive lattice vectors \mathbf{a}_1 and \mathbf{a}_2 with integer coefficients n_1 and n_2

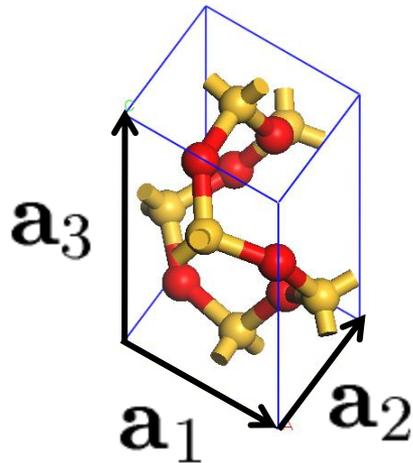
$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$$



Lattice with a basis

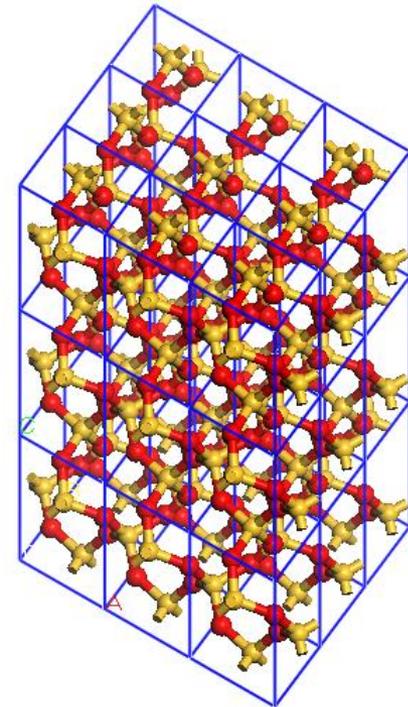
Example: alpha quartz (SiO_2)

The **simulation cell** with its primitive lattice vectors and its basis



- The lattice vectors define the Bravais lattice
- The atoms in each cell define the “basis” of the lattice (nothing to do with basis sets!)
- The basis is repeated at each lattice vector

The **crystal** is made from an infinite number of **simulation cells**



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

The reciprocal lattice

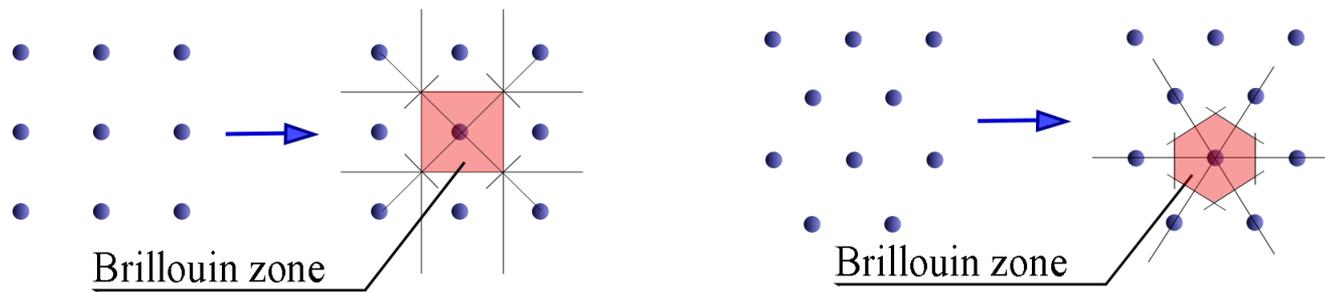
- A Bravais lattice by the **primitive reciprocal lattice vectors**:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

- The primitive reciprocal lattice vectors have the following property:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

- The 1st Brillouin zone (usually written as “1BZ”) is defined as the most symmetric unit cell of the reciprocal lattice. Examples:



- You can confirm that the volume of the reciprocal lattice unit cell is $2\pi/V_{\text{cell}}$ where V_{cell} is the volume of the direct lattice unit cell

Bloch's Theorem

- For wavefunctions for non-interacting electrons (“Molecular Orbitals”, MOs) in an external potential that has the periodicity of a Bravais lattice
- An external potential with lattice periodicity is unchanged by translation along any lattice vector $V_{\text{ext}}(\mathbf{r} + \mathbf{R}) = V_{\text{ext}}(\mathbf{r})$
- Bloch's theorem states that

The diagram shows the Bloch theorem equation $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$. The terms are circled in blue. Three pink boxes with arrows point to the terms: 'MO of entire crystal' points to $\psi_{\mathbf{k}}(\mathbf{r})$, 'A point within 1BZ' points to $e^{i\mathbf{k}\cdot\mathbf{r}}$, and 'MO with Bravais lattice periodicity' points to $u_{\mathbf{k}}(\mathbf{r})$.

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

MO of entire crystal

A point within 1BZ

MO with Bravais lattice periodicity

- We can therefore apply it in DFT calculations to solve for the Kohn-Sham orbitals of an entire (infinite) crystal by performing the calculation only in one simulation cell

Brillouin zone averages

- Due to Bloch's theorem each (spatial) molecular orbital does not only depend on its quantum number n , but also on the point \mathbf{k} in the 1BZ, so we represent it as

$$\psi_{n,\mathbf{k}}(\mathbf{r})$$

- The quantum number n is discrete, but \mathbf{k} is continuous, so quantities such as the density are obtained by **summation** over n but **integration** over \mathbf{k} , which is equivalent to averaging over the 1BZ

$$n(\mathbf{r}) = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{1BZ}} \left(\sum_{n=1}^{N_{\text{el}}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2 \right) d\mathbf{k} = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{1BZ}} \left(\sum_{n=1}^{N_{\text{el}}} |u_{n,\mathbf{k}}(\mathbf{r})|^2 \right) d\mathbf{k}$$

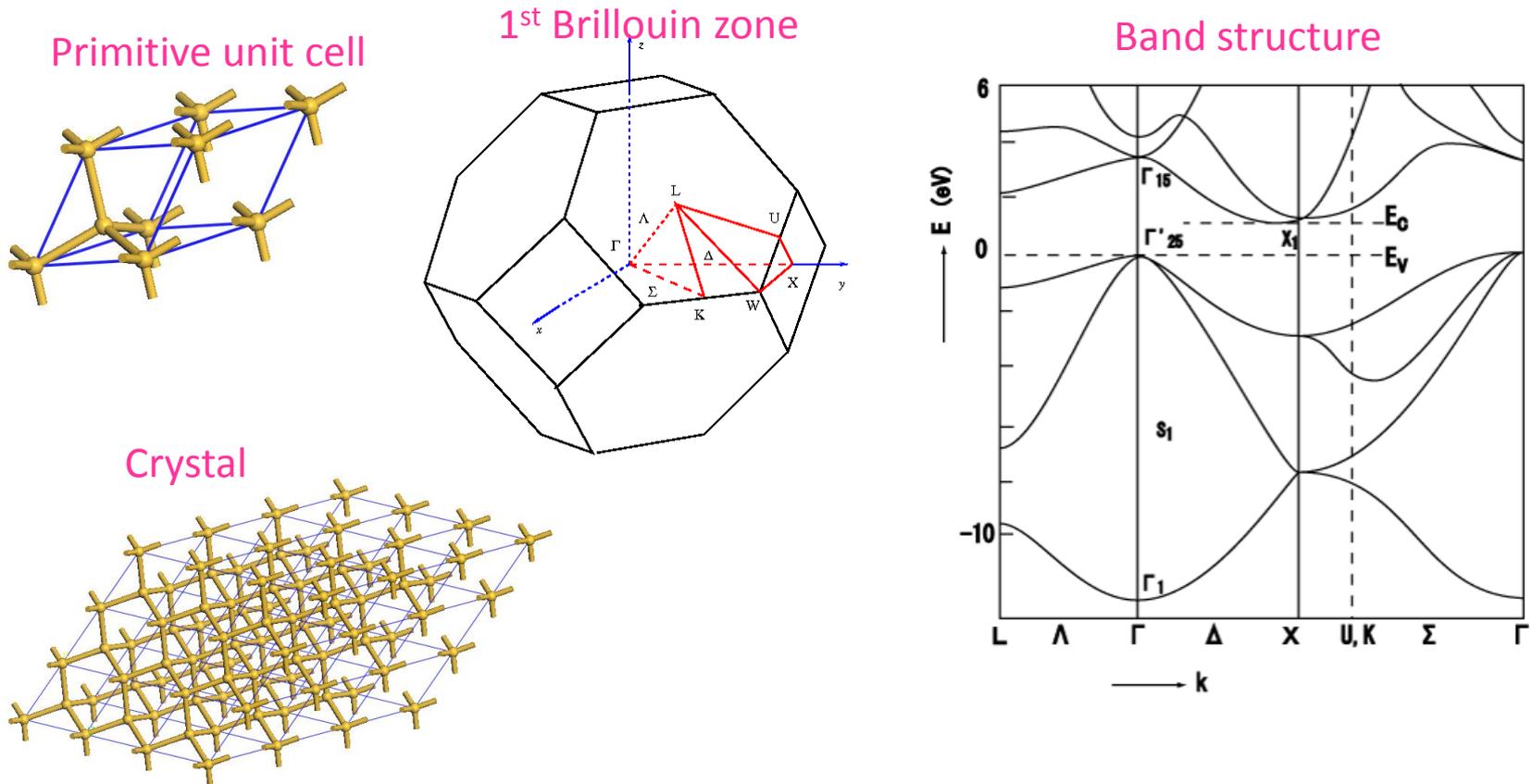
- The Kohn-Sham Hamiltonian also depends on \mathbf{k} and a different Kohn-Sham equation is solved for each \mathbf{k}

$$\hat{h}_{\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r}) = \varepsilon_{n,\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r})$$

- In practice, calculations are performed on a grid of points in 1BZ which are referred to as “**k**-points”

Example: band structure of crystalline silicon

- The eigenvalues $\epsilon_{n,\mathbf{k}}$ are called bands
- Many properties of a material can be deduced from its band structure, which shows the $\epsilon_{n,\mathbf{k}}$ as a function of \mathbf{k}



Plane wave basis set

- Plane waves are often used for calculations on materials
- The periodic Bloch functions are expanded in plane waves as follows:

$$u_{j,\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}| \leq G_{\max}} e^{i\mathbf{G} \cdot \mathbf{r}} C_{\mathbf{G};j,\mathbf{k}}$$

- The plane waves have by construction the same periodicity as the Bravais lattice because the \mathbf{G} vectors are reciprocal lattice vectors

$$\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$$

- The basis set is limited to all the plane waves with wavevector lengths less than some value G_{\max} , i.e. all vectors within a sphere of radius G_{\max}
- In practical calculations the basis set is input in terms of the “kinetic energy cut-off” value which is the energy of an electron in a periodic box as the unit cell and a plane wave wavefunction with wavevector of length G_{\max}

$$E_{\text{kin,cut}} = \frac{G_{\max}^2}{2}$$

Homework

- 1) Show that the plane waves as constructed in Slide 12 have the periodicity of the unit cell and are an orthogonal basis set
- 2) Write down the Kohn-Sham eigenvalue equation in plane-wave representation and show how it is more convenient to calculate the kinetic energy and Coulomb potential operators in reciprocal space and hence the need to use Fourier transforms

- 3) The following Fourier transform of a band $w_j(\mathbf{r} - \mathbf{R}) = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{1BZ}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{j,\mathbf{k}}(\mathbf{r}) d\mathbf{k}$ is called a Wannier function and

(in contrast to the bands that are delocalised over the entire crystal) it is localised in the unit cell of lattice vector \mathbf{R} . Show that the Wannier functions are an orthonormal set of functions (within the crystal) and then construct the opposite transformation, i.e. construct bands from the Wannier functions. In a similar way bands can be constructed from an localised Atomic Orbital (AO) basis set such as Gaussian basis functions.

5-minute quiz

Name :

Date :

Surname:

- 1) What is a crystal and what is a “simulation cell” or “primitive cell”?
- 2) Why do we need to consider the crystal and not just the unit cell in our calculations and how is this facilitated by Bloch’s theorem?
- 3) Show that the direct and reciprocal primitive lattice vectors obey the property $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$