

Theory of Semiconductor Devices (반도체 소자 이론)

Lecture 5

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Basic Quantum Mechanics

- An electron characterized by its **wavefunction**, $\psi(\mathbf{r})$, and *spin* orientation, \mathbf{s} , must satisfy the **time-independent Schrodinger equation**,

$$\mathbf{H}\psi(\mathbf{r}) = \mathcal{E}\psi(\mathbf{r}) \quad (2.1)$$

where \mathcal{E} is the **total energy** of the electron and \mathbf{H} is the appropriate ***Hamiltonian*** operator.

-The Hamiltonian takes into account all **kinetic** and **potential energy** terms, including applied **forces** and **interactions with other particles**.

- If the electron is traveling in a **force-free region** where it does not interact with other electrons (a **free electron**), the Hamiltonian contains only a kinetic energy term for the one electron, $\mathbf{p}^2/2m$, where the momentum operator, \mathbf{p} , is

$$\mathbf{p} = \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} = \frac{\hbar}{i} \nabla \quad (2.2)$$

and m is the free electron mass. In (2.2) $\hbar = h/2\pi$ where h is **Planck's constant**.

Basic Quantum Mechanics

- Under these conditions Schrodinger's equation (2.1) reduces to its free **one-electron formulation**,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \mathcal{E} \psi(\mathbf{r}) \quad (2.3)$$

which has **solutions** of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = A \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (2.4)$$

where \mathbf{k} is any **position-independent** vector.

- With these solutions we can easily determine the **free-electron energy** from (2.3) as

$$\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad (2.5)$$

- The **momentum** is determined by **operating** on (2.4) with (2.2) to give

$$\mathbf{p} = \hbar \mathbf{k} \quad (2.6)$$

Basic Quantum Mechanics

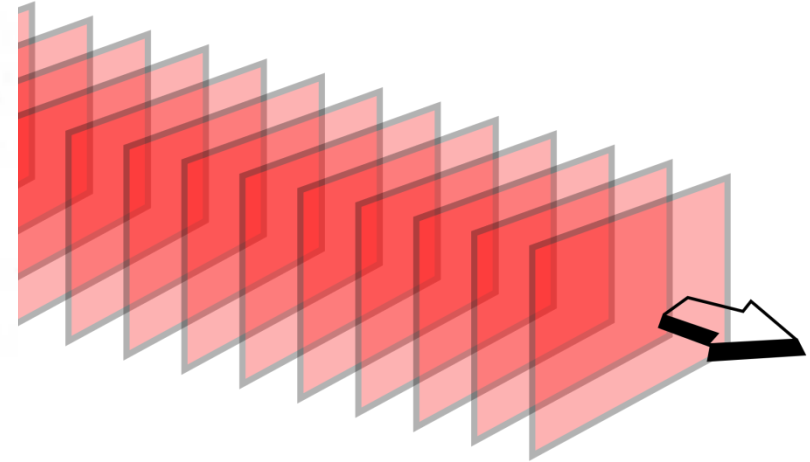
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Electron in a Potential

- Considering the electron as a particle with velocity $v = \mathbf{p}/m$, we arrive at the simple classical expression for the total energy of a free electron,

$$\mathcal{E} = \frac{\mathbf{p}^2}{2m} = \frac{1}{2} m v^2 \quad (2.7)$$

- From (2.4) we can also consider the electron as a **plane wave** with **wavevector \mathbf{k}** and **de Broglie wavelength**,

$$\lambda = \frac{2\pi}{|\mathbf{k}|} \quad (2.8)$$

- The problem we consider in this chapter is how this free-electron description is modified for electrons in a periodic crystal structure.

- We expect a **substantial modification** for the following reasons.

1. The **atoms in the crystal**, consisting of **valence** electrons, **core** electrons, and **nuclei**, produce a **potential energy** $U(\mathbf{r})$ with the **periodicity** of the direct Bravais lattice,

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}) \quad (2.9)$$

for all direct lattice vectors, \mathbf{R} .

2. Equation (2.8) tells us that a free-electron wavelength is of the **same order** of magnitude as the lattice periodicity. Thus we expect electrons to be **strongly diffracted** by the lattice.

One Electron Approximation

- To solve this problem, one would, *in principle*, have to include in the Hamiltonian of (2.1) terms that take into account **interactions** among the **nuclei**, **core electrons**, and **valence electrons**. Such a problem would be *difficult* to formulate, let alone solve.
- Since, in semiconductors the **valence electrons** are *shared among atoms*, a useful **approximation** is to **treat the valence electrons as non-interacting entities** that move through the crystal under the influence of an **effective potential** which includes the combined effects of the nuclei, the core electrons, and other valence electrons.
- Although not obvious a priori, this *one-electron approximation* provides a **good** description of semiconductor properties. In this manner we formulate a one electron Schrodinger equation from (2.1) and (2.9), where $U(\mathbf{r})$ is taken as an effective one-electron potential: that is, the potential that the nuclei, core electrons, and all the other valence electrons produce for one valence electron.
- The problem is then a manner of solving (2.1) for the allowed **one electron** energy levels.

One Electron Approximation

- There are several **reasons** why this **one-electron approximation works** as well as it does.

1. Electrons tend to be spatially removed from one another by **Coulomb repulsion** and by **Pauli exclusion** when they have the **same spin**. This **reduces the interaction** between the one electron and the rest of the valence electrons taken as a whole.
2. The valence electrons tend to **cluster around the ion cores** (nuclei and core electrons) due to **Coulomb attraction**. This effectively **screens** the Coulomb attraction of the ionic cores for the one electron and reduces this interaction.
3. Electrons passing near the ionic cores are **accelerated** by the Coulomb attraction. Because of this, electrons spend less time in the neighborhood of a core, effectively reducing the Coulomb attraction. (It is this effective **repulsion** that produces the **pseudopotential** discussed in Section 2.5.)

- For these reasons we will examine in detail **relatively simple one-electron models** that illustrate some of the more important properties of electrons **in periodic structures**. We then discuss the results of more detailed computations on **specific** crystal structures.

Bloch Electrons

Properties of electrons in periodic structures which are independent of the specific nature of the potential $U(\mathbf{r})$.

- **Bloch electron** : an electron that obeys the one-electron Schrodinger equation in a periodic potential.
- Bloch found that such electrons have *wavefunctions* in the form of a plane wave multiplied by a function that has the periodicity of the direct lattice. That is,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \quad (2.10)$$

where \mathbf{k} is a wavevector and

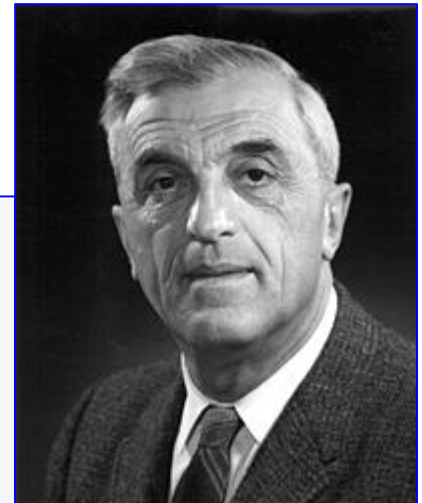
$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) \quad (2.11)$$

for all direct lattice vectors \mathbf{R} .

→ This result is known as **Bloch's theorem** [F. Bloch, *Z. Phys.* 52, 555 (1928)].

Felix Bloch (1905-1983)

He gained his doctorate in 1928. His doctoral thesis established the quantum theory of solids, using Bloch waves to describe the electrons. He and Edward Mills Purcell were awarded the 1952 Nobel Prize for "their development of new ways and methods for nuclear magnetic precision measurements.



Bloch Electrons

- From (2.10) we also have

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp [i\mathbf{k}\cdot(\mathbf{r} + \mathbf{R})]u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) \quad (2.12)$$

or using (2.11) ,

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp (i\mathbf{k}\cdot\mathbf{R})\psi_{\mathbf{k}}(\mathbf{r}) \quad (2.13)$$

for any value of \mathbf{k} and every \mathbf{R} in the direct lattice.

- Equation (2.13) : an alternative form of Bloch's theorem.

- It tells us that the electron wavefunction in any primitive unit cell of the direct lattice **differs** from that in any other cell **only by the factor** $\exp (i\mathbf{k}\cdot\mathbf{R})$. For real \mathbf{k} this represents a **difference in phase** as shown in Fig. 2. 1.

- We can see that this factor is similar to the expression obtained in (1.14), which was

$$\exp (i\mathbf{K}\cdot\mathbf{R}) = 1 \quad (2.14)$$

for all **reciprocal lattice vectors** \mathbf{K} . The wavevector, \mathbf{k} , thus has dimensions of reciprocal length and belongs in reciprocal space with the vectors \mathbf{K} . Let us assume, for instance, that some electron wavefunction has a **wavevector** that is equal to a reciprocal lattice vector.

Bloch Electrons

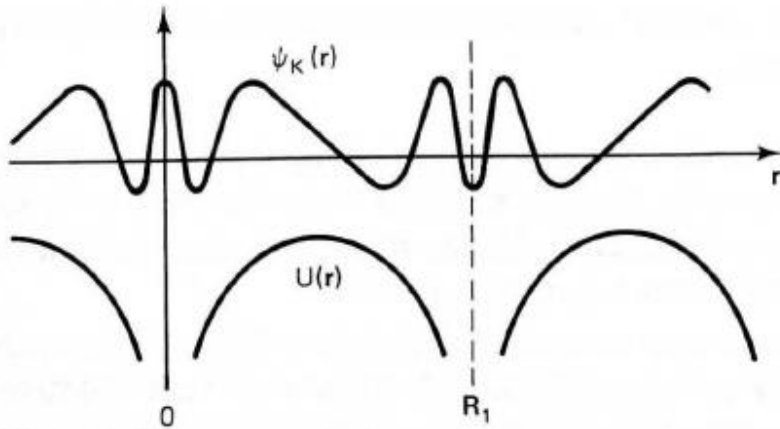


Figure 2.1 Possible Bloch electron wavefunction and periodic potential showing phase difference from one unit cell to the next. r and \mathbf{R}_1 are taken to be parallel.

From (2.13),

$$\begin{aligned}\psi_K(\mathbf{r} + \mathbf{R}) &= \exp(i\mathbf{K} \cdot \mathbf{R})\psi_K(\mathbf{r}) \\ &= \psi_K(\mathbf{r})\end{aligned}$$

for all \mathbf{R} . That is, **the electron wavefunctions ψ_K are periodic in \mathbf{R} .**

- Let us assume that an electron has a wavevector \mathbf{k} given by

$$\mathbf{k} = \mathbf{K} + \mathbf{k}' \quad (2.16)$$

where \mathbf{k}' is some **other vector** in reciprocal space. From (2.13) and (2.14) we find that

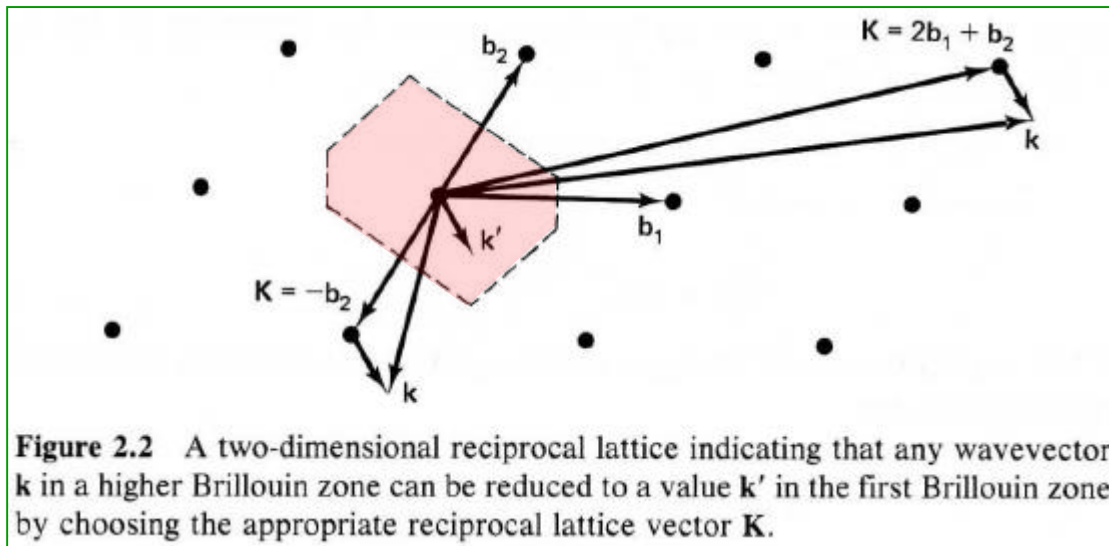
$$\begin{aligned}\psi_k(\mathbf{r} + \mathbf{R}) &= \exp\{i[(\mathbf{K} + \mathbf{k}') \cdot \mathbf{R}]\}\psi_k(\mathbf{r}) \\ &= \exp(i\mathbf{k}' \cdot \mathbf{R})\psi_k(\mathbf{r})\end{aligned} \quad (2.17)$$

or the wavefunctions ψ_k obey **Bloch's theorem** as if they had wavevector \mathbf{k}' .

-Thus the wavefunction **does not have a unique, wavevector \mathbf{k}** , but a set of wavevectors that differ from each other by the set of **reciprocal lattice vectors**.

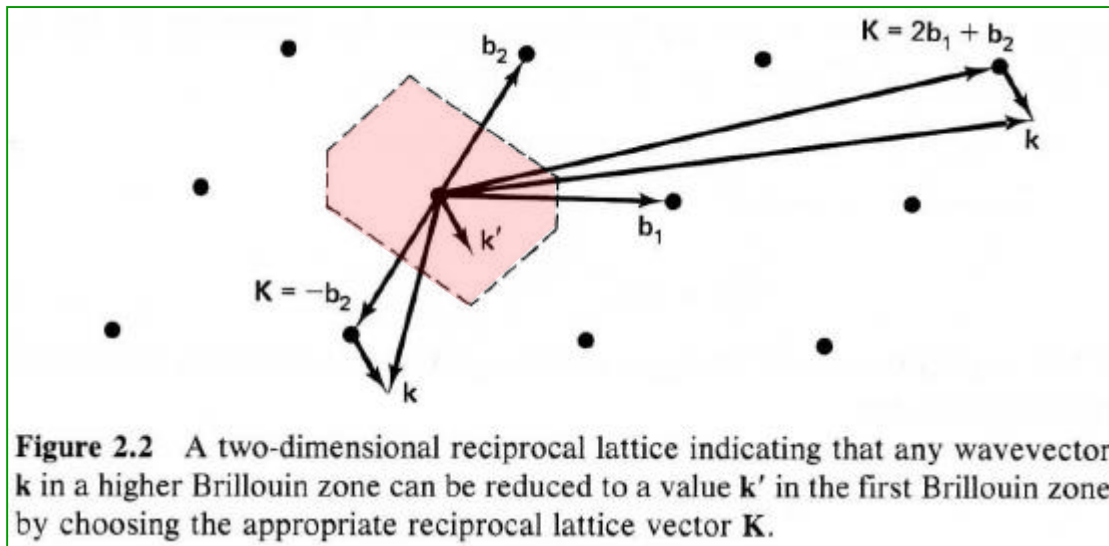
Bloch Electrons

- As indicated in Fig. 2.2, we can define a wavevector *uniquely* by reducing it with the *appropriate* reciprocal lattice vector *to the first Brillouin zone*.
- The prescription for this reduction is as follows.
- We choose the value of \mathbf{K} that will make the point \mathbf{k}' lie as **close to the origin** as is possible. Since the value of \mathbf{K} can be selected in increments of \mathbf{b}_i , the primitive vectors, the point \mathbf{k}' can be made to lie **closer to the origin** than to any other lattice point in reciprocal space. This, of course, is the first Brillouin zone.
- Therefore, we have shown that **any wavevector in higher Brillouin zones in reciprocal space is equivalent to one in the first Brillouin zone**. It is for this reason that the first Brillouin zone is to be preferred over other primitive unit cells in the reciprocal lattice.



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Bloch Electrons

Number of allowed values of \mathbf{k} in the first Brillouin zone

- This can be determined by introducing **boundary conditions** at the **outer surfaces of the crystal**.
- If there are a total of N **primitive unit cells** of volume Ω in a crystal of volume V so that $N\Omega = V$, the N unit cells can be divided into N_i unit cells in the directions of the \mathbf{a}_i primitive vectors, $i = 1, 2, 3$, so that

$$N = N_1 N_2 N_3 \quad (2.18)$$

- Thus the boundary of the crystal in the \mathbf{a}_i direction is at $N_i \mathbf{a}_i$.
- **To avoid standing electron waves** we impose a **cyclic** or Born-von Karman [M. Born and T. von Karman, *Z. Phys.* 13, 297 (1912)] condition at these boundaries,

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + N_i \mathbf{a}_i), \quad i = 1, 2, 3 \quad (2.19)$$

According to **Bloch's theorem** (2.13), we have

$$\psi_k(\mathbf{r} + N_i \mathbf{a}_i) = \exp(iN_i \mathbf{k} \cdot \mathbf{a}_i) \psi_k(\mathbf{r}) \quad (2.20)$$

or

$$\exp(iN_i \mathbf{k} \cdot \mathbf{a}_i) = 1 \quad (2.21)$$

Bloch Electrons

- Since the \mathbf{a}_i are **real**, the \mathbf{k} must also be **real** to satisfy (2.21) .
- If we **define** the wavevectors k in terms of the **primitive vectors** for the **reciprocal** lattice \mathbf{b}_i , we can write

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3 \quad (2.22)$$

$$\mathbf{b}_1 = \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3, \quad \mathbf{b}_2 = \frac{2\pi}{\Omega} \mathbf{a}_3 \times \mathbf{a}_1, \quad \mathbf{b}_3 = \frac{2\pi}{\Omega} \mathbf{a}_1 \times \mathbf{a}_2 \quad (1.16)$$

where the components k_i are **to be determined**.

- By inserting (1.16) for the \mathbf{b}_i into (2.22) and (2.22) into (2.21) , we obtain

$$\exp(i2\pi N_i k_i) = 1 \quad (2.23)$$

or

$$N_i k_i = m_i, \quad i = 1, 2, 3 \quad (2.24)$$

where the m_i takes on **all integer values** . Thus the **allowed values** of \mathbf{k} in **reciprocal** space are

$$\mathbf{k} = \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3 \quad (2.25)$$

- From (1.17) the **reciprocal lattice vector** which **defines** the reciprocal **lattice primitive unit cell** is

$$\mathbf{K} = \mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3 \quad (2.26)$$

and from (1.20) that the **volume** of this cell is

$$\Omega_K = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\Omega} \quad (2.27)$$

Bloch Electrons

- In a similar manner, the volume of reciprocal space occupied by an allowed value of k is defined by

$$\mathbf{k} = \frac{\mathbf{b}_1}{N_1} + \frac{\mathbf{b}_2}{N_2} + \frac{\mathbf{b}_3}{N_3} \quad (2.28)$$

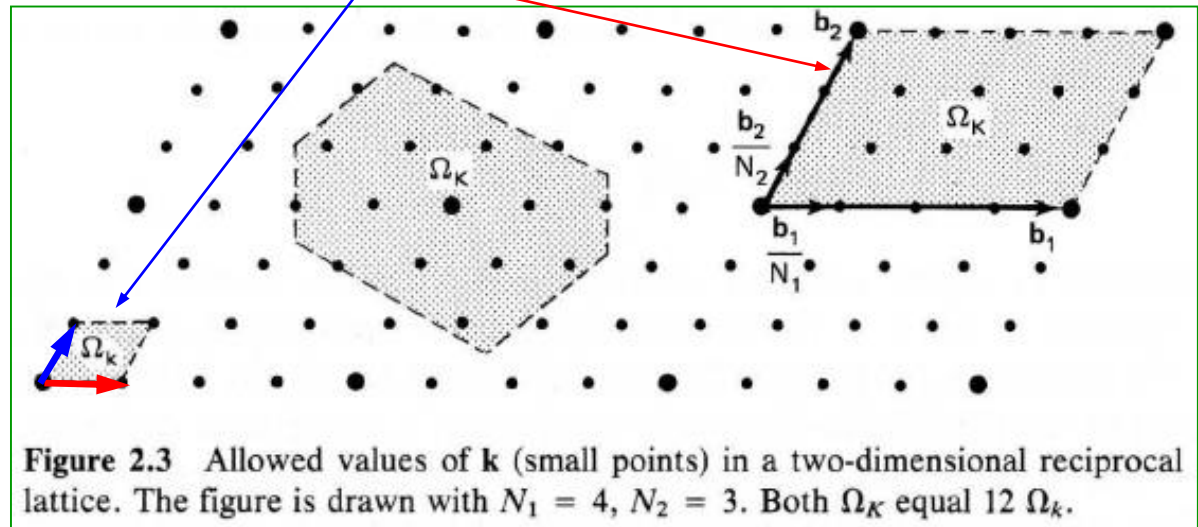
and given as

$$\Omega_k = \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3} \right) = \frac{(2\pi)^3}{N\Omega} = \frac{(2\pi)^3}{V} \quad (2.29)$$

Therefore,

$$\Omega_K = N\Omega_k \quad (2.30)$$

and since the volume of a primitive cell is *independent* of how it is chosen, there are N allowed values of \mathbf{k} in the first Brillouin zone.



Bloch Electrons

- Since the number of unit cells N in a crystal of volume V is equal to or has the same order of magnitude as the number of atoms (10^{22} to 10^{23} per cubic centimeter), the number of allowed values of k in the first Brillouin zone is quite large and Ω_k is very small.
- Because of this it is sometimes *convenient* to treat reciprocal space and the first Brillouin zone as a *continuum* for \mathbf{k} values.
- However, when \mathbf{k} is used to index the energy levels in each energy band, it is treated as discrete .
- It is interesting to compare the wavevector \mathbf{k} for Bloch electrons to the wavevector for free electrons. From (2.6) we know that for free electrons \mathbf{k} is proportional to the electron momentum,

$$\mathbf{p} = \hbar\mathbf{k} \quad (2.31)$$

Bloch Electrons

- For **Bloch electrons**, however, this is *not* the case.
- To determine the relationship between \mathbf{p} and \mathbf{k} for **Bloch electrons**, we operate on (2.10) with (2.2) to give

$$\mathbf{p}\psi_k(\mathbf{r}) = \hbar\mathbf{k}\psi_k(\mathbf{r}) + \exp(i\mathbf{k}\cdot\mathbf{r}) \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} u_k(\mathbf{r})$$

which for a periodic potential, is not a constant times the wavefunction.

- Thus $\hbar\mathbf{k}$ is **not** the momentum of a **Bloch electron**. It is, *nevertheless*, useful and convenient to define a **crystal momentum** for Bloch electrons as

$$\mathbf{P} = \hbar\mathbf{k} \quad (2.32)$$

We will find in Section 2.8 that this crystal momentum, \mathbf{P} behaves as a momentum **only for externally applied forces**.

- The "**real**" momentum, \mathbf{p} , *must* take into account the **response of the Bloch electrons** to **externally applied forces** and the **internal periodic potential** of the crystal.