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where

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \tag{8.4}$$

for all **R** in the Bravais lattice.[2]

Note that Eqs. (8.3) and (8.4) imply that

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r}). \tag{8.5}$$

Bloch's theorem is sometimes stated in this alternative form:[3] the eigenstates of H can be chosen so that associated with each ψ is a wave vector **k** such that

$$\boxed{\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}),} \tag{8.6}$$

for every **R** in the Bravais lattice.

We offer two proofs of Bloch's theorem, one from general quantum-mechanical considerations and one by explicit construction.[4]

FIRST PROOF OF BLOCH'S THEOREM

For each Bravais lattice vector **R** we define a translation operator $T_{\mathbf{R}}$ which, when operating on any function $f(\mathbf{r})$, shifts the argument by **R**:

$$T_{\mathbf{R}}f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}). \tag{8.7}$$

Since the Hamiltonian is periodic, we have

$$T_{\mathbf{R}}H\psi = H(\mathbf{r} + \mathbf{R})\psi(\mathbf{r} + \mathbf{R}) = H(\mathbf{r})\psi(\mathbf{r} + \mathbf{R}) = HT_{\mathbf{R}}\psi. \tag{8.8}$$

Because (8.8) holds identically for any function ψ, we have the operator identity

$$T_{\mathbf{R}}H = HT_{\mathbf{R}}. \tag{8.9}$$

In addition, the result of applying two successive translations does not depend on the order in which they are applied, since for any $\psi(\mathbf{r})$

$$T_{\mathbf{R}}T_{\mathbf{R}'}\psi(\mathbf{r}) = T_{\mathbf{R}'}T_{\mathbf{R}}\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R} + \mathbf{R}'). \tag{8.10}$$

Therefore

$$T_{\mathbf{R}}T_{\mathbf{R}'} = T_{\mathbf{R}'}T_{\mathbf{R}} = T_{\mathbf{R}+\mathbf{R}'}. \tag{8.11}$$

Equations (8.9) and (8.11) assert that the $T_{\mathbf{R}}$ for all Bravais lattice vectors **R** and the Hamiltonian H form a set of commuting operators. It follows from a fundamental theorem of quantum mechanics[5] that the eigenstates of H can therefore be chosen to be simultaneous eigenstates of all the $T_{\mathbf{R}}$:

$$\begin{aligned} H\psi &= \mathcal{E}\psi, \\ T_{\mathbf{R}}\psi &= c(\mathbf{R})\psi. \end{aligned} \tag{8.12}$$

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[2] The index n is known as the *band index* and occurs because for a given **k**, as we shall see, there will be many independent eigenstates.

[3] Equation (8.6) implies (8.3) and (8.4), since it requires the function $u(\mathbf{r}) = \exp(-i\mathbf{k}\cdot\mathbf{r})\,\psi(\mathbf{r})$ to have the periodicity of the Bravais lattice.

[4] The first proof relies on some formal results of quantum mechanics. The second is more elementary, but also notationally more cumbersome.

[5] See, for example, D. Park, *Introduction to the Quantum Theory*, McGraw-Hill, New York, 1964, p. 123.

The eigenvalues $c(\mathbf{R})$ of the translation operators are related because of the condition (8.11), for on the one hand

$$T_{\mathbf{R}'}T_{\mathbf{R}}\psi = c(\mathbf{R})T_{\mathbf{R}'}\psi = c(\mathbf{R})c(\mathbf{R}')\psi, \tag{8.13}$$

while, according to (8.11),

$$T_{\mathbf{R}'}T_{\mathbf{R}}\psi = T_{\mathbf{R}+\mathbf{R}'}\psi = c(\mathbf{R} + \mathbf{R}')\psi. \tag{8.14}$$

It follows that the eigenvalues must satisfy

$$c(\mathbf{R} + \mathbf{R}') = c(\mathbf{R})c(\mathbf{R}'). \tag{8.15}$$

Now let $\mathbf{a}_i$ be three primitive vectors for the Bravais lattice. We can always write the $c(\mathbf{a}_i)$ in the form

$$c(\mathbf{a}_i) = e^{2\pi i x_i} \tag{8.16}$$

by a suitable choice[6] of the x_i. It then follows by successive applications of (8.15) that if $\mathbf{R}$ is a general Bravais lattice vector given by

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \tag{8.17}$$

then

$$c(\mathbf{R}) = c(\mathbf{a}_1)^{n_1}c(\mathbf{a}_2)^{n_2}c(\mathbf{a}_3)^{n_3}. \tag{8.18}$$

But this is precisely equivalent to

$$c(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}, \tag{8.19}$$

where

$$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3 \tag{8.20}$$

and the $\mathbf{b}_i$ are the reciprocal lattice vectors satisfying Eq. (5.4): $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$.

Summarizing, we have shown that we can choose the eigenstates ψ of H so that for every Bravais lattice vector $\mathbf{R}$,

$$T_{\mathbf{R}}\psi = \psi(\mathbf{r} + \mathbf{R}) = c(\mathbf{R})\psi = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}). \tag{8.21}$$

This is precisely Bloch's theorem, in the form (8.6).

THE BORN–VON KARMAN BOUNDARY CONDITION

By imposing an appropriate boundary condition on the wave functions we can demonstrate that the wave vector $\mathbf{k}$ must be real, and arrive at a condition restricting the allowed values of $\mathbf{k}$. The condition generally chosen is the natural generalization of the condition (2.5) used in the Sommerfeld theory of free electrons in a cubical box. As in that case, we introduce the volume containing the electrons into the theory through a Born–von Karman boundary condition of macroscopic periodicity (page 33). Unless, however, the Bravais lattice is cubic and L is an integral multiple of the lattice constant a, it is not convenient to continue to work in a cubical volume of side L. Instead, it is more convenient to work in a volume commensurate with a

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[6] We shall see that for suitable boundary conditions the x_i must be real, but for now they can be regarded as general complex numbers.