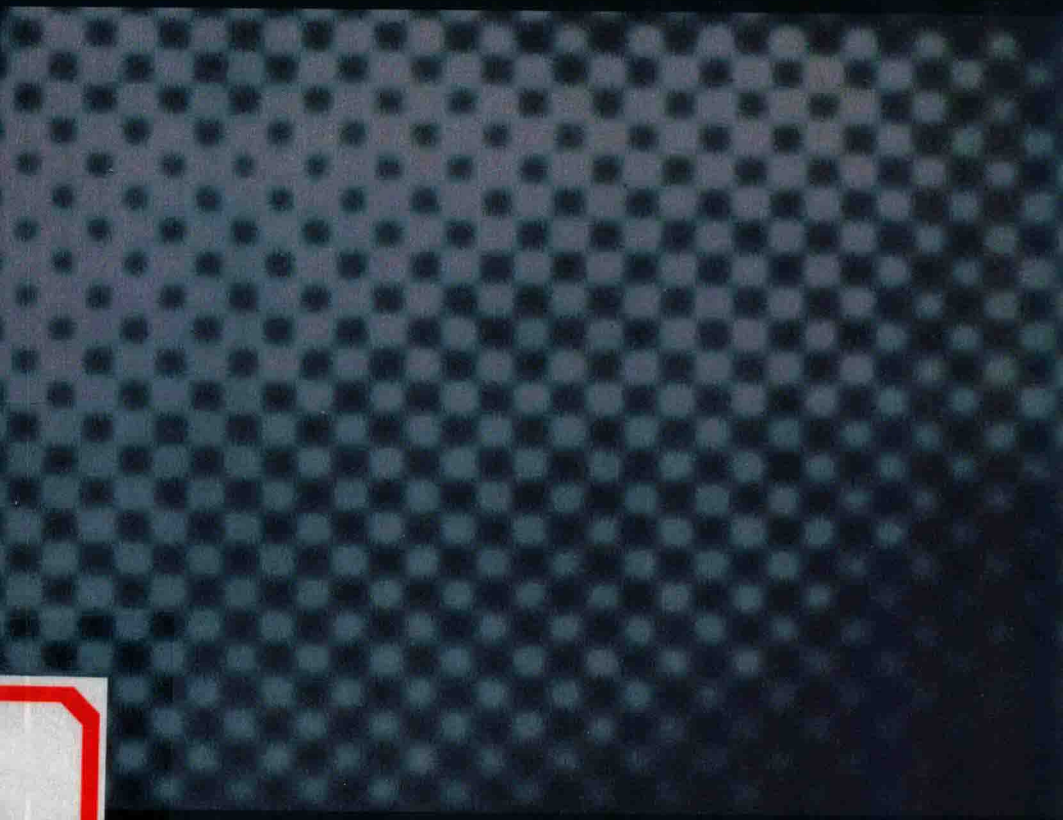
牛津大学研究生教材

固体量子理论

R. E. 佩尔斯



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固体量子理论

R. E. 佩尔斯　著

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影印版前言

自从上世纪80年代起，世界图书出版公司北京公司一直致力于与世界各国知名出版商合作，是国内最早开展购权影印图书出版工作的机构。时至今日，已经持续近30年，不仅引进的品种数独占鳌头，而且包括了大量在国际上具有深远影响的经典图书，受到了国内学者和专家的认可和好评。

现在应国内广大读者的要求，在获得牛津大学出社授权的前提下，世界图书出版公司北京公司将陆续影印出版该社各类丛书中的经典图书。牛津大学出版社是世界著名出版机构之一，每年出版的书籍、刊物超过四千种，其学术著作和教科书的作者均为相关领域的著名学者，其中不乏科学研究前沿的顶尖科学家和领军人物，书籍内容涵盖了最新的科学进展的各个方面，因此一直受到国内外科研人员和高校师生的高度评价，其中已经出版的数学和物理学系列丛书，如*Oxford Graduate Texts in Mathematics*，*Oxford Graduate Texts*，*Oxford Lecture Series in Mathematics and Its Applications*和*Oxford Mathematical Monographs*在国内有着广泛的影响，受到普遍好评。

毫无疑问，考虑到我国的国情以及科学教育发展的迫切需要，这项工作的最大受益者将是那些经济尚不富裕，但却渴望学习知识，想及时了解最新科学技术成果的国内高校和研究机构中的莘莘学子，相对原版，影印版的价格他们更容易接受。在这里，中国的读者和我们出版公司要特别感谢牛津大学出版社以传播科技知识为重，授权世界图书出版公司北京公司影印出版该社系列丛书中的部分图书。我们相信，这些图书的引进，不仅会受到数学物理等相关专业的教师和研究生的欢迎，相关领域的科研人员也将会从中受益。

前　言

固体量子理论有时被认为远不如现代理论物理学其他分支受到重视。持这种观点的原因在于，如果不采用简化或者不作近似，对所关注的多体系统的动力学问题将无法进行处理，而这些简化和近似往往忽略了问题的本质特征。然而，固体量子理论确实包含大量有内在兴趣的工作，基于它们或者可以发展出源自第一性原理的令人信服的一个解决方法，或者至少可以给出被忽略特性的一个清晰物理图像，从而定性地讨论他们可能引起的物理性质的变化。

在本书对固体量子理论的介绍中,我关注于一些基本的问题,在适当理想化的情况下求解它们的公认方法以及有待解决的一些重要基本问题.近期的文献往往关注于实际应用方面,包括特定物质性质的讨论,因此一些强调基本方面看上去是非常有用的.

本书首先面向于理论物理学工作者，同时也适用于具有一定量子力学基础，想要了解研究固体性质所常用模型基础知识的实验工作者。本书是在1953年为Les Houches（莱苏什）理论物理暑期学校（格勒诺布尔大学举办）开设课程所准备的讲义的基础上完成的。

书中内容的组织顺序以便于阐述而不是按照学科的发展史确定的。作者没有力图明确标出每种观点、方法的原作者，他们的名字可以在更详细的综述文章以及参考文献中引用的教科书中找到。

固体理论的一些分支已经取得了很大的进展，在这样一本小篇幅的著作中不可能将它们合理地都包含在内。特别是晶体结构和结合能、固体的强度和塑性以及电介质的电击穿这些重要的论题在本书中被完全省略了。

我要感谢Les Houches理论物理暑期学校的组织者，特别是其主任Cecile De Witt夫人的盛情邀请，给我提供一个机会来整理我对该课题的想法。与暑

期学校中许多成员的讨论，使得本书的某些论点表述得更为清晰. 伯明翰的几个研究生，尤其是J. B. Taylor, W. Marshall和D. A. Greenwood给了我很多建设性的意见，后者还很友好地参与了本书的校对。最后，感谢出版商在许多方面给我提供的帮助，同时也感谢那些我不知其名的校对员，他们在措辞方面给了许多有用的建议。

R. E. P.

伯明翰

1954年7月

重印说明

重印本没有做大的改动，只是改正了一些小错误，其中重要的几个出现在方程（7.30），（7.32），（7.34）和（7.40）中。感谢W. Pauli教授为我指出这些错误。

在第一、二、七、八章的末尾，增加了进一步的解释或者最近的参考文献。

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CRYSTAL LATTICES. GENERAL THEORY

1.1 Introduction. Examples of structures

By a solid we usually mean a substance which shows some stiffness under shear. Normally such substances have a crystalline structure, and, for the purposes of this book, we shall limit ourselves to crystalline solids. This excludes glasses, and I shall not discuss the question whether glasses should properly be regarded as solids, and which of our results, if any, may be applicable to them.

A crystal lattice may be constructed by repeating a 'unit cell', which may consist of one or more atoms, periodically. The vector leading from a point in one unit cell to the corresponding point in another is called a 'lattice vector' and can be represented as a linear combination with integral coefficients of a small number of basic lattice vectors. The set of lattice vectors determines the 'translation group' of the lattice. All lattices with the same translation group differ by having different unit cells; the simplest of them has just one atom in the unit cell. The translation group is therefore often specified by the name of this simplest lattice belonging to it.

I shall make no attempt to give a complete list of even the more important types of lattices, but I shall give a few examples, which will be used later as illustrations.

We start with cubic lattices, which are defined as remaining unchanged if rotated by 90° about any one of three mutually perpendicular axes. It is then clear that the basic lattice vectors can be stated most simply in relation to these cubic axes.

(*a*) *Simple cubic lattice.* The unit cell has a single atom, the basic lattice vectors are three vectors of equal length a in the directions of the three cubic axes. In other words, taking Cartesian coordinates along these axes, the basic lattice vectors are

$$(a, 0, 0), \qquad (0, a, 0), \qquad (0, 0, a),$$

the general lattice vector, and hence the position of any lattice point relative to a given one, being

$$(n_1 a, n_2 a, n_3 a)$$

with arbitrary integers (positive, negative, or zero) n_1, n_2, n_3.

(*b*) *Body-centred cubic lattice.* One atom per unit cell. Basic lattice vectors

$$(a, 0, 0), \quad (0, a, 0), \quad (0, 0, a), \quad (\tfrac{1}{2}a, \tfrac{1}{2}a, \tfrac{1}{2}a).$$

It is evident that two sector equals the sum of the other three, so that the most general point is either

$$(n_1 a, n_2 a, n_3 a)$$

or

$$((n_1+\tfrac{1}{2})a, (n_2+\tfrac{1}{2})a, (n_3+\tfrac{1}{2})a).$$

The first set of points forms a simple cubic lattice, the second consists of all the centres of the cubes formed by adjacent points of the first set, hence the name.

One can look at this lattice as having the translation group of the simple cubic lattice, and two atoms in the unit cell, and sometimes this may be convenient, but by doing so one obscures important relationships, because it looks as if the distance between the two atoms in the unit cell were arbitrary, whereas to preserve the cubic symmetry the lattice must be exactly as above.

(*c*) *Face-centred cubic lattice.* One atom per unit cell. Basic lattice vectors

$$(a, 0, 0), \quad (0, a, 0), \quad (0, 0, a), \quad (\tfrac{1}{2}a, \tfrac{1}{2}a, 0), \quad (\tfrac{1}{2}a, 0, \tfrac{1}{2}a).$$

The most general lattice point is

$$(n_1 a, n_2 a, n_3 a) \quad \text{or} \quad ((n_1+\tfrac{1}{2})a, (n_2+\tfrac{1}{2})a, n_3 a),$$

or $\quad ((n_1+\tfrac{1}{2})a, n_2 a, (n_3+\tfrac{1}{2})a) \quad$ or $\quad (n_1 a, (n_2+\tfrac{1}{2})a, (n_3+\tfrac{1}{2})a),$

or, expressed differently,

$$(\tfrac{1}{2}n_1 a, \tfrac{1}{2}n_2 a, \tfrac{1}{2}n_3 a),$$

with n_1, n_2, n_3 integers of which either one or all three are even, i.e. $n_1+n_2+n_3$ must be even. This lattice consists of a simple cubic one and added to it the centres of the faces of each cube. It has the property that, for given distance between neighbouring lattice points, the number of lattice points per unit volume is as large as possible. It is therefore called 'close-packed', because it describes an equilibrium arrangement of hard spheres packed tightly together.

These three lattices cover all the cubic translation groups.

(*d*) *Simple hexagonal lattice.* One atom per unit cell. The basic lattice vectors are two sides of an equilateral triangle, and a third vector at right angles to the plane of the first two. In Cartesian components

$$(a, 0, 0), \quad (\tfrac{1}{2}a, \tfrac{1}{2}\sqrt{3}a, 0), \quad (0, 0, b).$$

The ratio b/a is not restricted by the symmetry. The general lattice point is, accordingly,

$$((n_1+\tfrac{1}{2}n_2)a,\ \tfrac{1}{2}\sqrt{3}n_2 a,\ n_3 b),$$

or, expressed differently,

$$(n_1 . \tfrac{1}{2}a,\ n_2 . \tfrac{1}{2}\sqrt{3}a,\ n_3 b),$$

where n_1, n_2, n_3 are integers (positive, negative, or zero), such that n_1 and n_2 are either both even or both odd.

As an important example of a unit cell containing more than one atom, consider the NaCl type lattice. This is a simple cubic lattice in which alternate points are occupied by positive and negative ions (e.g. Na^+ and Cl^-) respectively. Since these are not identical, the translation group consists only of those displacements which lead from a positive to another positive ion. It is easy to see that this is the translation group of the face-centred cubic lattice, with a spacing equal to twice that of the simple cubic lattice occupied by all the ions together. Hence the unit cell may be taken to consist of

one positive ion at (0, 0, 0),

one negative ion at $(\tfrac{1}{2}a, 0, 0)$,

with the face-centred cubic translation group described above.

This gives the lattice sites

$(\tfrac{1}{2}n_1 a,\ \tfrac{1}{2}n_2 a,\ \tfrac{1}{2}n_3 a)$ for positive ions,

$(\tfrac{1}{2}(n_1+1)a,\ \tfrac{1}{2}n_2 a,\ \tfrac{1}{2}n_3 a)$ for negative ions,

again with the restriction that $n_1+n_2+n_3$ must be even. The second set can be covered by the same formula as the first, provided we take $n_1+n_2+n_3$ to be odd, and in this form it is evident that the sites of all ions form a simple cubic lattice of spacing $\tfrac{1}{2}a$.

Although in this case the unit cell contains two atoms, their spacing is not arbitrary, but is related to the cubic symmetry. If the positive ions were moved relatively to the negative ones, a structure of much lower symmetry would result.

As a further important example, consider the hexagonal close-packed structure. This is obtained from the simple hexagonal lattice by adding a further plane half-way between the original triangular networks, with lattice sites in the positions corresponding to the centres of one-half of the original triangles.

The unit cell now consists of atoms at

$$(0, 0, 0) \quad \text{and} \quad (\tfrac{1}{2}a,\ \tfrac{1}{6}\sqrt{3}a,\ \tfrac{1}{2}b),$$

so that the general lattice point becomes

$$(\tfrac{1}{2}n_1 a,\ \tfrac{1}{2}n_2\sqrt{3}a,\ n_3 b) \quad \text{and} \quad (\tfrac{1}{2}(n_1+1)a,\ \tfrac{1}{2}(n_2+\tfrac{1}{3})\sqrt{3}a,\ (n_3+\tfrac{1}{2})b).$$

The reason for having to use a unit cell of two atoms is that the distance between the two cannot be regarded as a lattice vector, since its repetition does not lead to a site occupied by another atom. As before, any alteration of the distance between the atoms in the unit cell, without changing the translation group, would reduce the symmetry. However, the ratio b/a is still arbitrary. For the particular value

$$b/a = \sqrt{\tfrac{8}{3}} = 1{\cdot}632$$

each atom is surrounded by twelve neighbours at the same distance. This again makes such a pattern suitable for packing hard spheres closely together, the density being, in fact, the same as for the close-packed cubic structure. This property accounts for the name of the lattice, but, unless we are actually dealing with hard spheres, the particular value of b/a is of no significance.

These examples may suffice to illustrate the description of lattices. In general, we have to specify the structure of the unit cell, containing r atoms, by listing their positions,†

$$\mathbf{d}_1,\ \mathbf{d}_2,\ldots,\ \mathbf{d}_r$$

relative to some origin in the unit cell, and to list the lattice vectors $\mathbf{a}_\mathbf{n}$, where the suffix $\mathbf{n}$ stands for a set of numbers as in the examples. The general position of a lattice point is then

$$\mathbf{d}_j+\mathbf{a}_\mathbf{n}. \tag{1.1}$$

Sometimes it is convenient to choose a unit cell larger than necessary, and then to have all translation vectors equal to integral combinations of three basic vectors, so that the lattice sites are

$$\mathbf{d}_j+n_1\mathbf{a}\ +n_2\mathbf{a}_2+n_3\mathbf{a}_3, \tag{1.2}$$

where the n's are arbitrary integers. For instance, in the body-centred cubic lattice described before, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are vectors of length a in the direction of the coordinate axes, and

$$\mathbf{d}_1 = (0,\ 0,\ 0), \qquad \mathbf{d}_2 = (\tfrac{1}{2}a,\ \tfrac{1}{2}a,\ \tfrac{1}{2}a).$$

1.2. Dynamical problem. Adiabatic approximation

We next turn to the question of the forces which hold the atoms at or near the sites of a regular crystal structure, and for this we first have to find variables in terms of which the problem can be stated.

† Symbols in bold type indicate vectors or tensors.

The atoms which constitute a solid consist of nuclei and electrons. For a description of the state of the solid it is not, however, necessary to specify the state of all the Z electrons of each atom, since we can eliminate most or all of them by a principle that is familiar from the theory of molecules.† Since the atomic nuclei are much heavier than the electrons, they move much more slowly, and it is therefore reasonable to start from the approximation in which they are taken to be at rest, though not necessarily in the regular positions. Then, if we use $\mathbf{R}$ as a symbol for all the position vectors of the N nuclei $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N$, we may imagine the Schrödinger equation solved for the motion of n electrons, with coordinate vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$, collective symbol $\mathbf{r}$, in the field of the nuclei in the configuration $\mathbf{R}$. The resulting wave function will be a function of the $3n$ variables $\mathbf{r}$, and contain $\mathbf{R}$ as parameters. The energy eigenvalue will similarly contain $\mathbf{R}$ as parameters. We may therefore define the lowest energy value $E_0(\mathbf{R})$ and the corresponding eigenfunction $\psi_0(\mathbf{r}, \mathbf{R})$. If we now go over to the real problem in which the nuclei are not held fixed, we may try the assumption that at any time the state of the electrons is described by the same wave function, inserting for $\mathbf{R}$ the positions of the nuclei at that time. We then merely have to describe the state of motion of the nuclei by a wave function $\phi(\mathbf{R})$, and therefore the wave function of the whole system appears in the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \phi(\mathbf{R}).\psi_0(\mathbf{r}, \mathbf{R}). \tag{1.3}$$

This is known as the 'adiabatic approximation', since the function $\psi_0(\mathbf{r}, \mathbf{R})$ represents the variation of the electronic state upon adiabatic changes of the parameters.

The condition for (1.3) to represent a good approximation to the solution of the complete Schrödinger equation is usually discussed in the theory of molecules, and one knows that the condition is

$$U\hbar/l \ll \Delta E, \tag{1.4}$$

where U is the velocity of the nuclei, $\hbar$ is Planck's constant divided by 2π, l is the distance by which the nuclei have to move to produce an appreciable change in $\psi_0(\mathbf{r}, \mathbf{R})$, and ΔE is the difference of the first excited electron level, at fixed $\mathbf{R}$, from the ground state. One verifies easily that for the inner electrons (e.g. the K shell) this condition is always satisfied.

It may be satisfied for all electrons. This can be the case when the solid is built of chemically saturated units. The simplest such case is that of a solid inert gas such as He, Ne, A,..., when the right-hand side is several electron volts, and the left-hand side considerably less. Another

† See, for example, Slater (1951), Appendix 18.

typical case is that of an ionic lattice like NaCl, in which each of the ions has again a closed-shell configuration. Another case covered by this approximation is that of a molecular solid, like solid H_2, in which each molecule has a saturated electron configuration and a finite excitation energy. A somewhat more complicated example is that of diamond, in which the carbon atoms seem to have homopolar bonds, as in an organic molecule, so that one may again regard the electron state as saturated, but cannot express this in terms of small saturated sub-units.

As an example in which the adiabatic approximation is bound to fail, consider the case of an alkali, like Na. Here each atom is unsaturated, in the sense that it contains a free spin, which is capable of two different orientations with the same energy. N atoms put together will therefore have 2^N states with very similar energies. (The energies will differ somewhat because of the interaction between the atoms, and this is a problem which we shall discuss in detail later on.) If there are that many states within a finite energy interval, their distances are bound to be negligibly small, and the inequality (1.4) cannot hold.

In such cases a complete description of the state of the system must include some electronic variables. It is sufficient, however, to include only the outer electrons in this description. Indeed, once we take away the valency electrons, the remaining ions will form closed shells without degeneracy and with a finite excitation energy. We may therefore, in general, apply the adiabatic approximation to the ions, and imagine the system described in terms of the positions of the ions and of the valency electrons.

In some cases the division between ion core and valency electrons may be ambiguous, or we may be in doubt whether the adiabatic approximation is valid for the last closed shell. We may then always include the electrons of that shell in our description, and we shall see that many qualitative conclusions, at any rate, are not affected by this.

The division I have sketched here is, of course, precisely the division between metals, which contain 'free' electrons, and non-metals, in which all electrons are part of saturated structures. It does not, however, follow that we can predict the nature of a solid immediately from the properties of the atom. For example, the reasoning given above for an alkali would not work if in fact it formed a molecular lattice. Molecular solid Na, in which pairs of atoms form saturated units, exists no doubt in principle, but it is less stable than the ordinary form. To be sure that alkalis are metals we must therefore either fall back on our empirical knowledge that in ordinary conditions they do not form molecular