

FROM FINITE TO INFINITE CRYSTALS: ANALYTIC
SOLUTION OF SIMPLE TIGHT BINDING MODEL
OF FINITE SC, FCC AND BCC CRYSTALS
OF ARBITRARY SIZE

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The electronic structure of finite sc, fcc and bcc crystals having a rectangular parallelepiped geometry is investigated here. In all three cases, analytic formulae for the energies and wave functions are obtained. It is shown that the results for the fcc and bcc lattice in the tight binding first nearest neighbour approximation can directly be obtained from those for the sc lattice in the third nearest neighbour approximation. Further it is shown for the crystals in question that the concept of the Brillouin zone has a good meaning not only for the infinite crystals but also for the finite ones. The mutual relation of real and Born-Kármán boundary conditions and the transition finite-infinite crystal in both directions are investigated and discussed in detail.

1. INTRODUCTION

The recent period has been a time of increasing interest in the theoretical investigation of physical properties of finite or semi-infinite crystals. The main reason for this is that the increasing number of experimental data concerning physical, chemical and structural properties of solid surfaces is in substantial advance of their theoretical explanation. Of all problems, a good understanding of the behaviour of electrons in finite crystals is of great importance in various areas, such as chemisorption, chemical reactions on surfaces, interpretation of spectroscopic and diffraction experiments on surfaces, surface magnetism, etc.

The infinite crystals discussed in the conventional solid state physics represent a useful idealization which gives an acceptable description not only of many important physical phenomena of large macroscopic crystals but even of the bulk properties of not very small clusters of atoms. However, there are relevant properties of finite crystals (e.g. those related to the surface) which cannot be explained in the framework of the infinite model at all. The calculation of the electronic structure of any real finite crystal is much more complicated than that of the infinite one. Two kinds of troubles slow down progress in this field: first, the existence of the surface and the lack of the translational symmetry make the solution of this problem difficult; second, comparison of the theory with experiments is rather questionable due to the excessive difference between real surfaces and their theoretical models. We are forced by these difficulties to replace the real crystal by a simplified physical model and in addition to that to find out its approximate mathematical solutions. The problem of the

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on noting that switching off some interactions, the sc crystal decomposes into two fcc or four bcc non-interacting lattices. Since these crystals do not interact, it is possible to take the sc crystal solutions at sites of the fcc or bcc crystal in question and thus obtain the results of interest. We show for the before-mentioned model that it is suitable to use the concept of the Brillouin zone not only for the infinite crystals but also for the finite ones, discuss the relation of real and Born-Kármán boundary conditions and investigate the transition finite-infinite crystal in both directions.

2. SUMMARY OF THE SC LATTICE RESULTS

The tight binding method according to which the wave function of the electron is assumed to be a linear combination of the atomic orbitals $\varphi(\mathbf{r} - \mathbf{r}_i)$

$$(1) \quad \varphi(\mathbf{r}) = \sum_i c_i \varphi(\mathbf{r} - \mathbf{r}_i)$$

leads to the matrix eigenvalue problem

$$(2) \quad Hc = ES c,$$

where H and S are the Hamiltonian and overlap matrix respectively and the eigen-vector c represents the wave function.

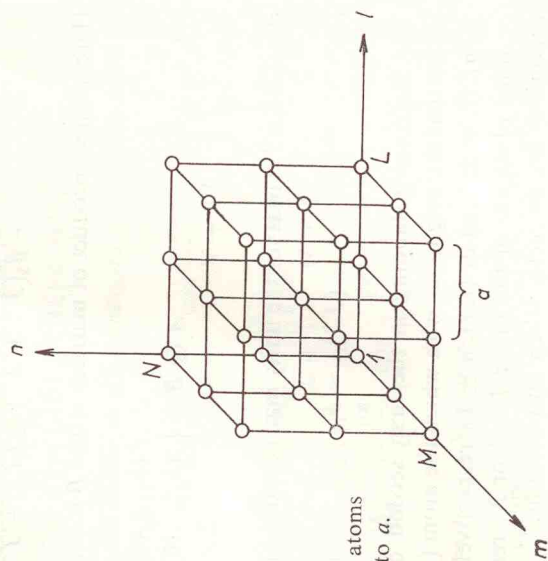


Fig. 1. The sc crystal with L , M and N atoms in edges. The lattice constant is equal to a .

Following work [3], we consider the sc crystal in the form of a finite rectangular parallelepiped with L , M and N atoms in edges (see Fig. 1). We give the site of an atom a) by three numbers (l, m, n) , $l = 1, \dots, L$; $m = 1, \dots, M$; $n = 1, \dots, N$ through which the site $\mathbf{r}_{lmn} = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$ is defined; \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 are the usual elementary vectors; b) by one number $s = l + (m - 1)L + (n - 1)LM$.

tronic properties of finite crystals has been attacked by various methods, most of them being adaptations of methods introduced and successfully verified in solid state theory or in quantum chemistry. The choice of the method is usually influenced by the nature of the problem under consideration.

When we investigate finite crystals one interesting and fundamental question arises: What are the changes of the energy levels and other relevant quantities when the crystal becomes infinite? Of course, it stands to reason that when increasing the number of atoms to the infinity the properties of the infinite solid must be obtained. Only a few investigations devoted to this convergence have been made till now [1-4]; the reason is that numerical calculations of the electronic structure cannot be carried out all over the range of the crystal size. The aim of this paper is to discuss a problem within a simple model of the crystal idealized in a degree enough to obtain analytic solutions (in [4], such a model is called an analytic cluster model). In fact, an analytic model of the finite crystal is the only one for which the transition to the infinite crystal can consistently be performed. In order to arrive at analytic solutions a number of approximations and restrictions must be made. The procedure used in the following discussion is: a) to use the tight binding method which seems to be most suitable because of a simple inclusion of the boundary conditions, b) to work within the one-band model (one atomic orbital per one atom), c) to consider the sc, fcc and bcc lattices, d) to assume a simple macroscopic shape of the crystal (the rectangular parallelepiped), e) to take into account interatomic interactions and overlap integrals up to a certain distance between atoms, f) to ignore the surface reconstruction. According to our opinion, the existence of analytic solutions balances a certain extent these rather drastic approximations.

Recently, only a few results regarding the analytic model of the electronic structure of the crystal with the sc lattice were known [1-5]. HOFFMANN [5] worked out the analytic results for the regular sc crystal in the LCAO nearest neighbour approximation. In [1], the "one-dimensional" (i.e. depending on the number of atoms in one dimension) convergence of the integrated and differential density of states in general and for the sc crystal in particular was established. The total energy of the sc crystal per atom shows the same behaviour. MESSMER [4] took into account nearest neighbour overlap integrals also and assumed different values of the matrix elements referred to the directions of three elementary vectors. BÍLEK and ŠKÁLA [2] generalized the results of MESSMER by taking into account the second nearest neighbours. They investigated the fcc lattice also and succeeded in giving results in the analytic form. ŠKÁLA [3] discussed the sc crystal with the third nearest neighbour interactions and showed that for further neighbours the simple set of solutions is lost.

In this work we summarize the sc results (section 2), derive using them the fcc and bcc solutions (section 3) which were partially given in [2] and discuss the bcc lattice (section 4). In the Appendix, we generalize the results of sections 2-4 for the case of non-zero overlap. Our method of obtaining the fcc and bcc formulae is based

We assume one s -like function $\varphi(\mathbf{r} - \mathbf{r}_i)$ localized on each atom and the interaction to the third nearest neighbours

$$\begin{aligned}
 H_{ii} &= \alpha, \\
 H_{ij} &= \beta_1 \text{ for the first nearest neighbours,} \\
 &\beta_2 \text{ for the second nearest neighbours,} \\
 &\beta_3 \text{ for the third nearest neighbours,} \\
 &0 \text{ otherwise.}
 \end{aligned}$$

the sake of simplicity, no change of the matrix elements near the surface of the crystal is assumed here.

Using the numeration b), the following very simple formula for the Hamiltonian matrix can be obtained

$$\begin{aligned}
 H &= \alpha I \otimes I \otimes I + \beta_1 [(J^+ + J^-) \otimes I \otimes I + I \otimes (J^+ + J^-) \otimes I + \\
 &+ I \otimes I \otimes (J^+ + J^-)] + \beta_2 [(J^+ + J^-) \otimes (J^+ + J^-) \otimes I + \\
 &+ (J^+ + J^-) \otimes I \otimes (J^+ + J^-) + I \otimes (J^+ + J^-) \otimes (J^+ + J^-)] + \\
 &+ \beta_3 (J^+ + J^-) \otimes (J^+ + J^-) \otimes (J^+ + J^-).
 \end{aligned}$$

Therefore, a direct product of matrices A and B is defined as

$$A \otimes B = \begin{pmatrix} Ab_{11}, Ab_{12}, \dots \\ Ab_{21}, Ab_{22}, \dots \\ \dots \end{pmatrix},$$

where symbol I stands for the unity matrix and "shift" matrices J^+ and J^- are given by

$$(J^+)_{ij} = \delta_{i+1,j}, \quad (J^-)_{ij} = \delta_{i,j+1}.$$

Matrix J^+ stands in the first, second or third place in the direct product with the neighbour with which the atom (l, m, n) interacts is at the site $(l \pm 1, m), (l, m \pm 1, n)$ or $(l, m, n \pm 1)$, respectively. All matrices on the first, second or third place are of the order L, M or N , respectively. In Eq. (4) the boundary conditions are correctly taken into account.

For the sake of simplicity we assume in the next that the overlap matrix S is the identity matrix (the generalization for the case $S \neq I$ is straightforward and is discussed in the Appendix). The solution of the eigenvalue problem (2) can be then found simply since the solution of a more simple problem

$$(J^+ + J^-) u = \lambda u$$

is well known (see e.g. [6]). For the eigenvalue problem of the order L , the eigenvalues and eigenvectors are given by

$$\lambda_p = 2 \cos \frac{p\pi}{L+1}, \quad p = 1, \dots, L,$$

and

$$u_p = \sqrt{\frac{2}{L+1}} \begin{pmatrix} \sin \frac{p\pi}{L+1} \\ \sin \frac{2p\pi}{L+1} \\ \vdots \\ \sin \frac{Lp\pi}{L+1} \end{pmatrix}, \quad p = 1, \dots, L.$$

Now we use the numeration b) and assume the eigenvector c in the form

$$c^{par} = u_p \otimes v_q \otimes w_r.$$

Here, u_p is given by Eq. (9) and v_q or w_r are given by the analogous expression for the eigenproblem of the order M or N , respectively. Making use of the relation

$$(A \otimes B \otimes C)(D \otimes E \otimes F) = (AD) \otimes (BE) \otimes (CF)$$

and of Eqs. (7)–(9) we easily obtain the corresponding energies

$$\begin{aligned}
 E_{par} &= \alpha + 2\beta_1 \left(\cos \frac{p\pi}{L+1} + \cos \frac{q\pi}{M+1} + \cos \frac{r\pi}{N+1} \right) + \\
 &+ 4\beta_2 \left(\cos \frac{p\pi}{L+1} \cos \frac{q\pi}{M+1} + \cos \frac{p\pi}{L+1} \cos \frac{r\pi}{N+1} + \right. \\
 &\left. + \cos \frac{q\pi}{M+1} \cos \frac{r\pi}{N+1} \right) + 8\beta_3 \cos \frac{p\pi}{L+1} \cos \frac{q\pi}{M+1} \cos \frac{r\pi}{N+1},
 \end{aligned}$$

$$p = 1, \dots, L; \quad q = 1, \dots, M; \quad r = 1, \dots, N.$$

When the numeration a) is used, the component of the eigenvector c^{par} on the atom (l, m, n) equals

$$c_{lmn}^{par} = \sqrt{\frac{8}{(L+1)(M+1)(N+1)}} \left[\sin \frac{l p \pi}{L+1} \sin \frac{m q \pi}{M+1} \sin \frac{n r \pi}{N+1} \right].$$

The eigenvectors c^{par} form the orthonormal set. Now we compare our formula for the energy (12) with the result of the usual tight binding approximation to the third

rest neighbours for the infinite crystal

$$E(k_x, k_y, k_z) = \alpha + 2\beta_1(\cos ak_x + \cos ak_y + \cos ak_z) + 4\beta_2(\cos ak_x \cos ak_y + \cos ak_x \cos ak_z + \cos ak_y \cos ak_z) + 8\beta_3 \cos ak_x \cos ak_y \cos ak_z.$$

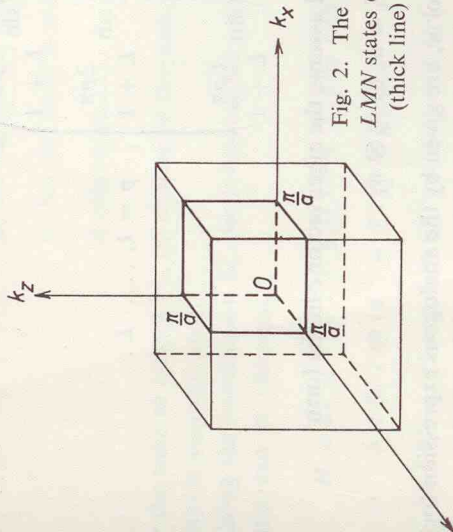


Fig. 2. The discrete wave vectors k_{pqr} giving all LMN states of the finite sc crystal lie in one eighth (thick line) of the first Brillouin zone (thin line).

if we define the points in the reciprocal k -space by

$$k_{pqr} = \left(\frac{p\pi}{(L+1)a}, \frac{q\pi}{(M+1)a}, \frac{r\pi}{(N+1)a} \right),$$

in dispersion relations (12) and (14) become the same and to each state (p, q, r) corresponds just one point k_{pqr} . Note that all points k_{pqr} lie in one eighth of the first Brillouin zone of the infinite crystal (see Fig. 2). This may seem to be accidental here, however, we show in the following sections that the same is true also in the case of the fcc and bcc lattices.

3. THE FCC LATTICE

In this section we investigate the electronic structure of a finite fcc crystal in the form of a rectangular parallelepiped. We numerate the sites in the same way as in section 2. For the sake of simplicity, we assume that L, M and N are odd (see section 3).

In order to obtain the solution of the eigenvalue problem (2) in this case it is important to notice that assuming the interactions to the second nearest neighbours only, for $\beta_1 = \beta_3 = 0$ and $\beta_2 \neq 0$, the sc crystal decomposes into two non-interacting

fcc crystals [2]. One of them is shown in Fig. 3 for $L = M = N = 3$, the other complementary one consists of unoccupied lattice sites. The matrix element $\beta_2 \equiv \beta$ stands, of course, for the interaction to the first nearest neighbours in the fcc lattice.

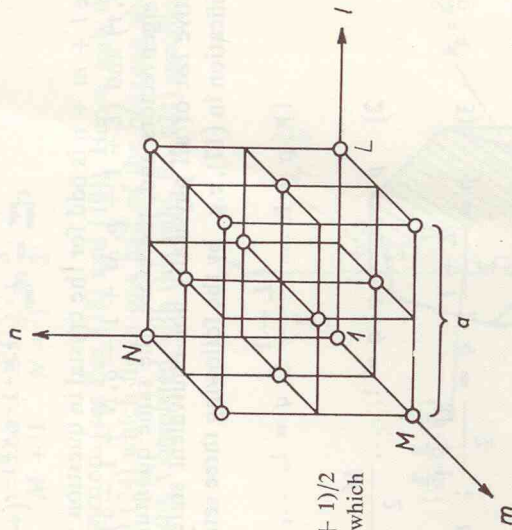


Fig. 3. The fcc crystal with $(LMN+1)/2$ atoms. Atoms are at the sites for which $l+m+n$ is odd.

Since both above-mentioned sublattices do not mutually interact, it follows that those components of the eigenvector (13) related to the sites of one sublattice only represent (except for the normalizing factor) the solution for the fcc crystal in question. Thus, for the crystal in Fig. 3 we have the following orthonormal eigenvectors

$$c_{lmn}^{pqr} = \sqrt{\frac{16f^{pqr}}{(L+1)(M+1)(N+1)}} \sin \frac{l p \pi}{L+1} \sin \frac{m q \pi}{M+1} \sin \frac{m r \pi}{N+1},$$

$$f^{pqr} = 1 + \delta_{2p-1, l} \delta_{2q-1, M} \delta_{2r-1, N},$$

$$l = 1, \dots, L; \quad m = 1, \dots, M; \quad n = 1, \dots, N; \quad l + m + n = \text{odd}.$$

The only problem which remains to be discussed is which of the eigenvalues

$$E_{pqr} = \alpha + 4\beta \left(\cos \frac{p\pi}{L+1} \cos \frac{q\pi}{M+1} + \cos \frac{p\pi}{L+1} \cos \frac{r\pi}{N+1} + \cos \frac{q\pi}{M+1} \cos \frac{r\pi}{N+1} \right),$$

$$p = 1, \dots, L; \quad q = 1, \dots, M; \quad r = 1, \dots, N$$

correspond to the eigenvectors (16). This can be most easily clarified taking notice

It is well known that for the infinite crystal only a half of the surface of the Brillouin zone yields physically non-equivalent states. Similarly, for the finite one some pairs of quantum states (p, q, r) satisfying the relation

$$(24) \quad \frac{p}{L+1} + \frac{q}{M+1} + \frac{r}{N+1} = \frac{3}{2}$$

give the same energies and wave functions (see Eqs. (18) and (19)). Hence, only those points \mathbf{k}_{pqr} given by Eqs. (22) and (24) which lie in one half of the hexagon shown in Fig. 4 must be taken into account. Completed with this rule, Eq. (21) specifies all

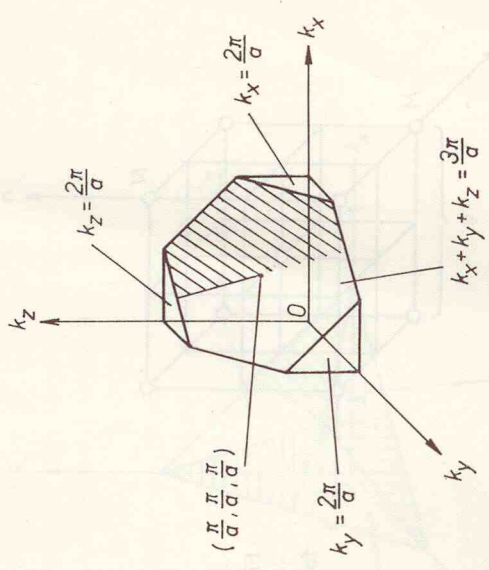


Fig. 4. In the same way as in the case of the sc crystal the discrete wave vectors \mathbf{k}_{pqr} giving all states of the fcc crystal lie in one eighth of the first Brillouin zone.

non-equivalent states described by Eq. (17). Concerning the other surfaces of one eighth of the Brillouin zone for which k_x, k_y , or k_z equals zero or $2\pi/a$, for any finite L, M and N there are no points \mathbf{k}_{pqr} belonging to them. Thus, these surfaces need not be taken into consideration here.

4. THE BCC LATTICE

Now we shall discuss the electronic structure of a finite crystal in the form of a rectangular parallelepiped with the bcc lattice. We numerate the lattice sites in the same way as in section 2. For the sake of simplicity we assume again that L, M and N are odd (see Fig. 5). The calculation and the discussion of the electronic structure of the bcc crystal can be carried out by analogy with the case of the fcc crystal.

First we note that for $\beta_1 = \beta_2 = 0$ the sc crystal decomposes into four non-interacting bcc crystals, one of them being shown in Fig. 5 for $L = M = N = 3$. Then the matrix element $\beta_3 \equiv \beta$ corresponds to the first nearest neighbour interaction in the bcc lattice.

relations

$$E_{pqr} = E_{L+1-p, M+1-q, N+1-r}$$

$$c_{lmm}^{pqr} = c_{lmm}^{L+1-p, M+1-q, N+1-r} (-1)^{l+m+n+1}$$

where $l + m + n$ is odd for the crystal in question we see that the quantum numbers (l, r) and $(L + 1 - p, M + 1 - q, N + 1 - r)$ designate the same eigenvalues eigenvalues and, therefore, the same quantum state. In order to give the extensive list of all physically non-equivalent states (p, q, r) we must replace their definition in (17), e.g., by the following three sets of admissible values

- 1) $p = 1, \dots, \frac{L-1}{2}; q = 1, \dots, M; r = 1, \dots, N;$
- 2) $p = \frac{L+1}{2}; q = 1, \dots, \frac{M-1}{2}; r = 1, \dots, N;$
- 3) $p = \frac{L+1}{2}; q = \frac{M+1}{2}; r = 1, \dots, \frac{N+1}{2}.$

total number of states given by Eq. (20) is correctly equal to the total number of states $(LMN + 1)/2$. Some energies can be, depending on L, M and N , highly degenerate. For example, the degeneracy of the level $E = \alpha$ is equal at least to $(M + N - 1)/2$. It is interesting that this quantity is just the number of surface atoms lying on three edges of the crystal which intersect at one corner.

In addition to Eq. (20) there is also another way of the specification of all non-equivalent states (p, q, r) which seems to be much more instructive from the point of view of comparison of finite and infinite crystals. Let us define the admissible states by means of the inequality

$$\frac{p}{L+1} + \frac{q}{M+1} + \frac{r}{N+1} \leq \frac{3}{2}$$

obtaining in the analogous way as in section 2

$$\mathbf{k}_{pqr} = \left(\frac{2p\pi}{(L+1)a}, \frac{2q\pi}{(M+1)a}, \frac{2r\pi}{(N+1)a} \right)$$

represent the states (p, q, r) as points in the reciprocal \mathbf{k} -space. By analogy with the sc crystal, the points for which Eq. (21) is fulfilled lie in one eighth of the first Brillouin zone shown in Fig. 4. The equality sign in Eq. (21) corresponds to the surface of the zone for which [7]

$$k_x + k_y + k_z = \frac{3\pi}{a}$$

Using the same approach as in section 3 we obtain the components of the orthogonalized eigenvectors for the bcc crystal in question (Fig. 5) in the form

$$c_{lmn}^{par} = \sqrt{\left[\frac{32|f^{par}|}{(L+1)(M+1)(N+1)} \right] \sin \frac{l p \pi}{L+1} \sin \frac{m q \pi}{M+1} \sin \frac{n r \pi}{N+1}},$$

$$f^{par} = 1 + \delta_{2p-1, L} \delta_{2q-1, M} + \delta_{2p-1, L} \delta_{2r-1, N} + \delta_{2q-1, M} \delta_{2r-1, N},$$

$$l = 1, \dots, L; \quad m = 1, \dots, M; \quad n = 1, \dots, N;$$

l, m, n are even or l, m, n are odd.

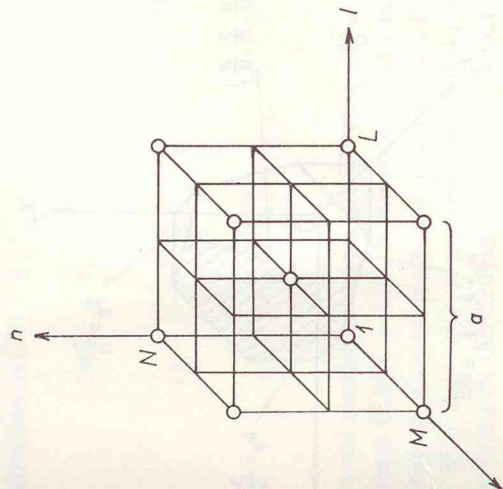


Fig. 5. The bcc crystal with $(LMN + L + M + N)/4$ atoms. Atoms are at the sites for which all l, m, n are even or all l, m, n are odd.

corresponding energies are given by the relation

$$E_{par} = \alpha + 8\beta \cos \frac{p\pi}{L+1} \cos \frac{q\pi}{M+1} \cos \frac{r\pi}{N+1}.$$

To the specification of the admissible values of quantum numbers p, q and r , the properties of trigonometric factors in Eqs. (25) and (26) must be analyzed. It follows from them that the exhaustive enumeration of all physically non-equivalent states given by two following sets

$$1) \quad p = 1, \dots, \frac{L+1}{2}; \quad q = 1, \dots, \frac{M+1}{2}; \quad r = 1, \dots, \frac{N+1}{2}$$

$$2) \quad p = \frac{L+3}{2}, \dots, L; \quad q = 1, \dots, \frac{M-1}{2}; \quad r = 1, \dots, \frac{N-1}{2}.$$

"centre of the band" $E = \alpha$ is at least $(LM + LN + MN + 1)/4$ -fold degenerate.

This quantity is equal to the number of surface atoms on three faces of the crystal intersecting at one corner.

A different way of the specification of the quantum numbers p, q and r is an employment of the concept of the Brillouin zone on the analogy of two preceding sections. In order to prevent multiple inclusion of the same state the positive integers p, q and r must fulfil some restricting conditions. Let us consider the inequalities

$$(28) \quad \frac{p}{L+1} + \frac{q}{M+1} \leq 1, \quad \frac{p}{L+1} + \frac{r}{N+1} \leq 1, \quad \frac{q}{M+1} + \frac{r}{N+1} \leq 1.$$

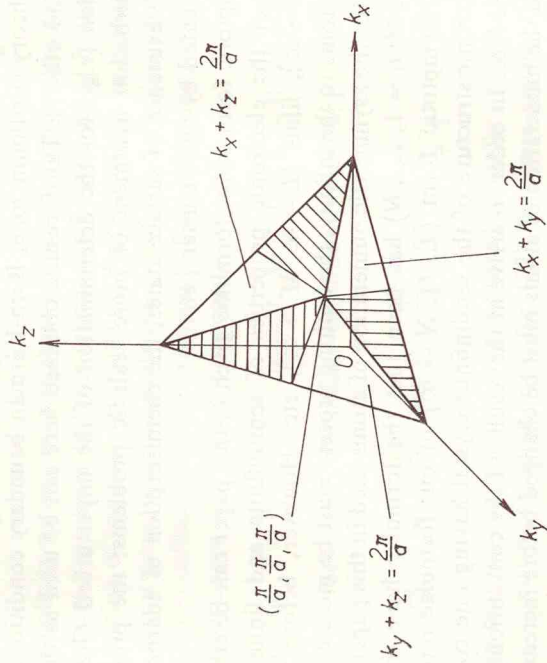


Fig. 6. The wave vectors k_{par} determining all $(LMN + L + M + N)/4$ states of the bcc crystal lie in one eighth of the first Brillouin zone.

Defining the discrete k -vectors by Eq. (22) we see that all points k_{par} corresponding to Eq. (28) lie in the part of the Brillouin zone shown in Fig. 6. The equalities in Eq. (28) correspond to the surfaces of the zone [7] for which

$$(29) \quad k_x + k_y = \frac{2\pi}{a}, \quad k_x + k_z = \frac{2\pi}{a}, \quad k_y + k_z = \frac{2\pi}{a}.$$

Just as for the infinite crystal, only a part of the surface of one eighth of the Brillouin zone yields non-equivalent quantum states (see Fig. 6). If one respects the preceding fact then Eqs. (25) and (26) completed with either Eq. (27) or Eq. (28) represent the complete analytic description of the electronic structure of the finite bcc crystal in question. It stands to reason that the total number of states $(LMN + L + M + N)/4$ is equal to the number of atoms in the crystal.

5. DISCUSSION

Despite of the considerable simplicity of the model investigated here (see the specifications a)–f) in the Introduction) the analytic description of the electronic structure of finite sc, fcc crystals of arbitrary size obtained in sections 2–4 can be valuable in many applications. First, it makes it possible to examine the behaviour of many physical quantities as a function of the size, macroscopic shape and symmetry of the crystal systematically going from one atom to the infinite solid. Second, the careful study of the limiting process finite-infinite crystal gives a new insight into the significance and justification of a number of concepts established in the conventional solid state theory (Brillouin zone, Born-Kármán boundary conditions, translational symmetry and others). Third, results obtained here can be used as the zeroth order approximation (e.g., for the determination of the unperturbed Green's function) the perturbation treatment of more realistic problems: the properties of real surfaces, the existence of surface states, the chemisorption of adatoms on the substrate represented by finite clusters, etc.

The asymptotic form of the formulae given in this paper can be employed for the description of the electronic properties of semiinfinite and finite systems such as rods ($L \rightarrow \infty$), films ($L \rightarrow \infty, M \rightarrow \infty$), etc. However, before increasing the number of atoms to the infinity, the limiting process must be more exactly specified. The reason for the asymmetric numeration of atoms used in this paper ($l = 1, \dots, L; n = 1, \dots, M; n = 1, \dots, N$) has been that the formulae have then a compact form. The asymptotic form ($L, M, N \rightarrow \infty$) of our formulae represents in this sense the electronic structure of the semiinfinite crystal having one corner and three semiinfinite edges. In order to arrive at the results of the conventional model of the infinite solid the numeration of atoms must be changed before increasing the dimensions to the infinity. Namely, the growth of the crystal must be considered with respect to its "geometrical" centre

$$\left(\frac{1}{2}(L+1), \frac{1}{2}(M+1), \frac{1}{2}(N+1)\right).$$

First, let us consider the transition from the infinite to finite crystal. For the infinite sc crystal the energy levels $E(k_x, k_y, k_z)$ worked out within the same approximation are given by Eq. (14) and the corresponding components of unnormalized eigenvalues are

$$c_{lmn}(k_x, k_y, k_z) = \exp(ik_x l a) \exp(ik_y m a) \exp(ik_z n a).$$

Concerning the fcc and bcc crystals similar results can be obtained (see [7]). For the sake of simplicity of the following discussion all formulae (including Eq. (30)) will refer to the sc lattice; for the fcc and bcc crystals the discussion is analogous, the lattice constant a , however, must be replaced by $a/2$. The mutual affinity between the energies $E(k_x, k_y, k_z)$ and finite crystal eigenvalues E_{par} is evident (compare Eqs. (14) and (14)). On the other hand, the character of the eigenvalues for finite and

infinite crystals is rather different. The reason for this is the presence of surfaces which is reflected by the form of boundary conditions. The usual and well-tried way of the quantization of the infinite crystal eigenstates is the application of the Born-Kármán cyclic boundary conditions [7]

$$(31) \quad \psi(\mathbf{r}) = \psi(\mathbf{r} + G_1 \mathbf{a}_1 + G_2 \mathbf{a}_2 + G_3 \mathbf{a}_3),$$

which yield the following admissible values of the wavevector \mathbf{k}

$$(32) \quad p = -\frac{G_1}{2} + 1, \dots, \frac{G_1}{2}; \quad q = -\frac{G_2}{2} + 1, \dots, \frac{G_2}{2}; \quad r = -\frac{G_3}{2} + 1, \dots, \frac{G_3}{2}.$$

For the sake of simplicity we assume here that G_1, G_2 and G_3 are even integers.

The transition from the infinite to finite crystal can be performed in the following way. The wavefunction of the electron inside the finite crystal is in general different from zero; however, it goes to zero outside the crystal. In our case, it follows from Eqs. (1)–(3) that the coefficients in the expansion of the wavefunction (1) are equal to zero just one layer above the surface of the crystal, i.e.

$$(33) \quad c_{lmn} = 0 \quad \text{for } l = 0, L + 1; \quad m = 0, M + 1; \quad n = 0, N + 1.$$

In sections 2–4 just these "zero boundary conditions" were applied to derive the eigenvalues

$$(34) \quad c_{lmn}^{par} = \sin l \frac{p\pi}{L+1} \sin m \frac{q\pi}{M+1} \sin n \frac{r\pi}{N+1}.$$

It is easy to verify that the coefficients (34) considered formally on the set $l, m, n = \dots, -1, 0, 1, \dots$ satisfy, in addition to Eq. (33), the more general "zero cyclic boundary conditions"

$$(35) \quad c_{lmn} = 0 \quad \text{for } l = i(L+1); \quad m = j(M+1); \quad n = k(N+1),$$

where i, j and k are arbitrary integers. Hence, putting the coefficients (34) into Eq. (1) we obtain the wavefunction ψ^{par} for which the condition similar to Eq. (31) holds

$$(36) \quad \psi^{par}(\mathbf{r}) = (-1)^{(ip+jq+kr)} \psi^{par}(r + i(L+1)\mathbf{a}_1 + j(M+1)\mathbf{a}_2 + k(N+1)\mathbf{a}_3).$$

Comparing Eqs. (36) and (31) we see that both conditions become the same if

$$(37) \quad G_1 = 2(L+1), \quad G_2 = 2(M+1), \quad G_3 = 2(N+1),$$

i.e., when we assume that the Born-Kármán domain (the rectangular parallelepiped part of the infinite crystal with dimensions $G_1 a \times G_2 a \times G_3 a$) includes eight identical non-interacting finite crystals (for the one-dimensional case see Fig. 7). It is worth taking notice of the fact that the integers G_1, G_2 and G_3 are even for any L, M and N .

Using Eq. (37) we obtain from Eq. (32) the wavevector components

$$(38) \quad k_x = \frac{p}{L+1} \frac{\pi}{a}, \quad k_y = \frac{q}{M+1} \frac{\pi}{a}, \quad k_z = \frac{r}{N+1} \frac{\pi}{a},$$

quantized in the case of the infinite crystal by

$$(39) \quad p = -L, \dots, L+1; \quad q = -M, \dots, M+1; \quad r = -N, \dots, N+1.$$

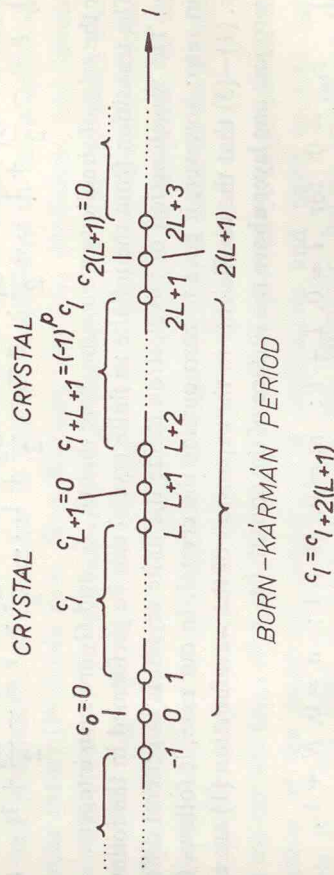


Fig. 7. The period in the Born-Kármán boundary conditions includes two identical non-interacting finite crystals and two atoms for which $c_l = 0$ (the one-dimensional case). These two atoms are the reason for the appearance of the unity in the expression $k_x = p\pi/[L+1]a$. This basic domain must be considered because of the change of the sign of the wave function in two neighbouring crystals when p is odd.

We note that expressing the finite crystal eigenvalues E_{par} by means of Eq. (38) they will coincide with $E(k_x, k_y, k_z)$. However, for finite crystals the quantization (39) must be replaced by (see sections 2-4)

$$(40) \quad p = 1, \dots, L; \quad q = 1, \dots, M; \quad r = 1, \dots, N.$$

The difference between Eqs. (39) and (40) is in a very close relation to the construction of the reduced Brillouin zone described in sections 2-4. This can be understood as follows.

For the infinite crystal the relation

$$(41) \quad E(k_x, k_y, k_z) = E(\pm k_x, \pm k_y, \pm k_z)$$

is valid (see Eqs. (12), (17) and (26)). In contrast to the energies, however, the coefficients $c_{lmn}(\pm k_x, \pm k_y, \pm k_z)$ (see Eq. (30)) corresponding to different signs of the vector components give, in general, eight linearly independent wave functions. Thus, the eigenvalues $E(k_x, k_y, k_z)$ are eight-fold degenerate and, to obtain the complete description of the electronic spectrum, the full Brillouin zone must be considered (see Eqs. (38) and (39)). For the finite crystal, equation (41) remains valid. In addition

to that, if we change the sign of some component of the \mathbf{k} -vector, all coefficients (34) rewritten as

$$(42) \quad c_{lmn}^{par} = c_{lmn}(k_x, k_y, k_z) = \sin(k_x l a) \sin(k_y m a) \sin(k_z n a)$$

simultaneously change the sign, i.e., the corresponding wave functions relate to the same quantum state. Thus, the eight-fold degeneracy of energy levels disappears and from the point of view of both energies and wave functions it is quite sufficient to consider one eighth of the first Brillouin zone, for example that one lying in the octant $k_x, k_y, k_z > 0$ (compare with Eq. (40)). In contrast to Eq. (39), the quantum numbers $p = 0, L+1; q = 0, M+1; r = 0, N+1$ are not included in Eq. (40), because they lead to the zero expansion coefficients $c_{lmn} \equiv 0$, i.e. they do not give any quantum state of the finite crystal.

There is one thing to be remarked about the reduction of the Brillouin zone to its one eighth. Owing to the symmetry properties of formula (42), the choice of any other octant in the reciprocal space instead of that used in sections 2-4 is equivalent. In addition, working with the \mathbf{k} -vectors defined as follows

$$(43) \quad \mathbf{k}_{par} = \left((-1)^p \frac{p\pi}{(L+1)a}, (-1)^q \frac{q\pi}{(M+1)a}, (-1)^r \frac{r\pi}{(N+1)a} \right),$$

we arrive at the full Brillouin zone, however, with eight times less density of states in the reciprocal space and, unfortunately, with the \mathbf{k} -point distribution not reflecting the point symmetry of the crystal lattice. Thus, the former definitions seem to be most natural and practical ones.

It is apparent from the above analysis that the zero periodical boundary conditions (35) are equivalent to the usual Born-Kármán boundary conditions completed by the requirements

$$(44) \quad c_{0mn} = c_{l0n} = c_{lm0} = 0 \quad \text{for all } l, m \text{ and } n.$$

For the infinite crystal, the Bloch-like solutions (30) can never satisfy Eq. (44), but it can be easily shown that the "standing wave" - type eigenvector (42) is just the convenient linear combination of the solutions (30) which fulfils the zero boundary conditions (35). The meaning of the conditions (44) is in a decomposition of the infinite crystal into a set of non-interacting finite ones. Taking then the wave function regarding one finite crystal only we get immediately the results of the preceding sections. It follows from here that all the results given in sections 2-4 may directly be obtained from those worked out for the infinite crystal when applying the usual tight binding method, Born-Kármán conditions and Eq. (44). The relation between the Born-Kármán periods and the dimensions of the crystal follows from Eq. (37). The preceding discussion can be comprehended, at least to a certain extent, to be a justification of the Born-Kármán boundary conditions usually being understood as rather artificial ones.

Now we turn briefly to the opposite transition from the finite to infinite crystal. In the tight binding approximation, all electronic properties of the infinite crystal can be described either a) by means of the asymptotic form ($L, M, N \rightarrow \infty$) of the results given in this paper or b) using the standard solid state theory directly applied to the infinite sample. Both approaches a) and b) are not fully equivalent, since they work with different boundary conditions (see the discussion above). Bearing in mind that any real crystal has in fact finite dimensions the first approach a) seems to be more adequate. On the other hand, when we investigate bulk properties of very large finite crystals, both approaches converge to the same results so that there is no reason why the elegant solid state theory of infinite crystals should not be used. We have assumed in sections 3 and 4 that L, M and N are odd. This assumption is not substantial, since the results for the other cases can easily be obtained on the analogy with the procedure used in this paper (see also [2] where some fcc results for an arbitrary L, M and N were given).

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APPENDIX

In sections 2-4, we have assumed that the overlap matrix S is the unity matrix. In the case of the non-zero overlap integrals can easily be taken into account. Assume in the same way as in Eq. (4)

$$\begin{aligned} (A 1) \quad S &= I \otimes I \otimes I + s_1 [(J^+ + J^-) \otimes I \otimes I + I \otimes (J^+ + J^-) \otimes I + \\ &+ I \otimes I \otimes (J^+ + J^-)] + s_2 [(J^+ + J^-) \otimes (J^+ + J^-) \otimes I + \\ &+ (J^+ + J^-) \otimes I \otimes (J^+ + J^-) + I \otimes (J^+ + J^-) \otimes (J^+ + J^-)] + \\ &+ s_3 (J^+ + J^-) \otimes (J^+ + J^-) \otimes (J^+ + J^-), \end{aligned}$$

where s_1, s_2 and s_3 are the overlap integrals for the first, second and third nearest neighbours, respectively, and making use of Eqs. (7)-(11) we easily find the energies of the sc crystal

$$(A 2) \quad E_{par} = \frac{\alpha + 2\beta_1 x_1^{par} + 4\beta_2 x_2^{par} + 8\beta_3 x_3^{par}}{1 + 2s_1 x_1^{par} + 4s_2 x_2^{par} + 8s_3 x_3^{par}}$$

where,

$$(A 3) \quad x_1^{par} = \cos \frac{p\pi}{L+1} + \cos \frac{q\pi}{M+1} + \cos \frac{r\pi}{N+1},$$

$$(A 4) \quad x_2^{par} = \cos \frac{p\pi}{L+1} \cos \frac{q\pi}{M+1} + \cos \frac{p\pi}{L+1} \cos \frac{r\pi}{N+1} + \\ + \cos \frac{q\pi}{M+1} \cos \frac{r\pi}{N+1},$$

$$(A 5) \quad x_3^{par} = \cos \frac{p\pi}{L+1} \cos \frac{q\pi}{M+1} \cos \frac{r\pi}{N+1}.$$

The eigenvectors (13) remain unchanged except for the normalizing factor. The energies of fcc and bcc crystals can be obtained from Eqs. (A 2)-(A 5) as it has been done in sections 3 and 4. All conclusions regarding the Brillouin zone and others remain valid.

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