LCAO WAVE-FUNCTIONS AND ENERGIES FOR CUBIC CRYSTALS
I. SIMPLE-CUBIC LATTICE

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The technique and results of calculations of the LCAO orbitals, being the basis functions of the total symmetry representation of the cubic point group, and the corresponding energies are presented in detail for the case of a simple cubic lattice with interaction between nearest-neighbour atoms. Models of four, five and seven sub-bands have been taken into account. The density of states per unit energy range has been calculated and compared with the results of Bloch in the cases of the nearest-neighbour atomic interaction and the almost-free electron approximation.

1. The equation and its solution

Our purpose is to solve the Wannier-Slater eigenequation [1, 2] for a simple cubic lattice. The solutions are the coefficient functions for the LCAO orbitals of a simple-cubic (sc) crystal. Only solutions being the basis functions of the total symmetry representation (Γ_1) of the cubic point group are of interest, because the electron density and its dependence on energy can be analyzed at only one lattice site representing the other sites, and this site can be put at the center of the coordinate system [3].

The Wannier-Slater (WS) operator for the sc lattice with one (s) kind of atomic orbital is

$$\hat{W}_{sc} = \sum_{m=0}^{m=\infty} \frac{1}{3(2m)!}\left(\frac{\partial^{2m}}{\partial X^{2m}} + \frac{\partial^{2m}}{\partial Y^{2m}} + \frac{\partial^{2m}}{\partial Z^{2m}}\right) =$$

$$= \frac{1}{3}\left[\cos\left(i\frac{\partial}{\partial X}\right) + \cos\left(i\frac{\partial}{\partial Y}\right) + \cos\left(i\frac{\partial}{\partial Z}\right)\right]. \tag{1}$$

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The number of terms in (1) extends to infinity, but in numerical practice, of course we take only a few terms. Our purpose is to find such A that the WS eigenequation

$$\hat{W}_{sc}A = \varepsilon A \tag{2}$$

is fulfilled. The quantity ε is a transform of the electron energy E in the crystal:

$$\varepsilon = \frac{E - E^0 - \gamma}{q\beta} \tag{3}$$

where E^0 is the eigenenergy of the atomic state (s), q the number of nearest-neighbour atoms, and γ and β are the respective interaction integrals,

$$\int \varphi^*(\boldsymbol{r} - \boldsymbol{R}_\mu)[V(\boldsymbol{r}) - U(\boldsymbol{r} - \boldsymbol{R}_\nu)]\varphi(\boldsymbol{r} - \boldsymbol{R}_\nu)d\tau, \tag{4}$$

for two cases: (i) $\boldsymbol{R}_\mu = \boldsymbol{R}_\nu$, and (ii) $\boldsymbol{R}_\mu$ is the nearest neighbour of $\boldsymbol{R}_\nu$. φ is the atomic orbital and U the atomic potential. In the case of the s atomic orbitals the integral (4) is equal for all nearest neighbours.

The first term in (1) is a constant, and the second is the Laplace operator. We try to find A in the form of the eigenfunctions of the Laplace operator; at the same time, the eigenfunctions should be the basis for the total-symmetry irreducible representation of the cubic point group. Thus $A \equiv A^{\Gamma_1}$ consist of terms of the form

$$(KH)^{\Gamma_1}_{l,t} j_l(\kappa R) \tag{5}$$

where κ is a parameter entering into the energy

$$\varepsilon(\kappa) = \sum_{i=0}^{i=\infty} \alpha_i \kappa^{2i} \tag{6}$$

and $(KH)^{\Gamma_1}_{l,t}$ are the non-normalized cubic harmonics of the representation Γ_1 [4, 5].[1]

We try to combine (5) in such a way that (2) is fulfilled for the largest possible number of terms included in W_{sc}; at the same the coefficients in the power series of $\varepsilon(\kappa)$ have to be determined.

The general technique by which equation (2) can be solved has been outlined in [3]. For the present case it seems to be best to illustrate it on an example. We seek to satisfy (2) for the polynomials:

const;	κ^2;	κ^4;
$\kappa^2 R^2$;	$\kappa^4 R^2$;	$\kappa^6 R^2$;
$\kappa^4 R^4$;	$\kappa^6 R^4$;	$\kappa^8 R^4$;
$\kappa^4(X^4+Y^4+Z^4)$;	$\kappa^6(X^4+Y^4+Z^4)$;	$\kappa^8(X^4+Y^4+Z^4)$;

[1] In the calculations $(KH)^{\Gamma_1}_6$ is assumed equal 3 times the corresponding non-normalized expression given in Refs. [4, 5], *i.e.* we have put

$$(KH)^{\Gamma_1}_6 = \left(\frac{X}{R}\right)^6 + \left(\frac{Y}{R}\right)^6 + \left(\frac{Z}{R}\right)^6 - \frac{15}{11}(KH)^{\Gamma_1}_4 - \frac{3}{7}.$$

$$
\begin{array}{lll}
\kappa^6 R^6; & \kappa^8 R^6; & \kappa^{10} R^6; \\
\kappa^6 R^2(X^4+Y^4+Z^4); & \kappa^8 R^2(X^4+Y^4+Z^4); & \kappa^{10} R^2(X^4+Y^4+Z^4); \\
\kappa^6(X^6+Y^6+Z^6); & \kappa^8(X^6+Y^6+Z^6); & \kappa^{10}(X^6+Y^6+Z^6); \\
\kappa^6 R^6; & \kappa^{10} R^8; & \kappa^{12} R^8; \\
\kappa^8 R^4(X^4+Y^4+Z^4); & \kappa^{10} R^4(X^4+Y^4+Z^4); & \kappa^{12} R^4(X^4+Y^4+Z^4); \\
\kappa^8 R^2(X^6+Y^6+Z^6); & \kappa^{10} R^2(X^6+Y^6+Z^6); & \kappa^{12} R^2(X^6+Y^6+Z^6); \\
\kappa^8(X^8+Y^8+Z^8); & \kappa^{10}(X^8+Y^8+Z^8); & \kappa^{12}(X^8+Y^8+Z^8);
\end{array} \tag{7}
$$

where

$$R^2 = X^2+Y^2+Z^2. \tag{8}$$

If A^{Γ_1} is expressed as a combination of the terms in (7), then the terms of the first column can arise on the left-hand side of (2) only as a result of multiplication of A^{Γ_1} by a constant, say 1; those of the second column — from the same multiplication and the action of the Laplace operator; and those of the third column — from the multiplication mentioned and the action of the Laplace operator together with that of the operator $\frac{\partial^4}{\partial X^4}+\frac{\partial^4}{\partial Y^4}+\frac{\partial^4}{\partial Z^4}$. The combinations of (7) which are at our disposal, and can be then introduced into A^{Γ_1}, are chosen as

$$j_0(\kappa R) \equiv (KH)_0^{\Gamma_1} j_0(\kappa R) \tag{9a}$$

and

$$(KH)_4^{\Gamma_1} j_4(\kappa R),\ (KH)_6^{\Gamma_1} j_6(\kappa R) \text{ and } (KH)_8^{\Gamma_1} j_8(\kappa R). \tag{9b}$$

In A^{Γ_1} the coefficient at $j_0(\kappa R)$ is put equal to 1; the coefficients at the functions (9) are disposable parameters.

Since the first term on the left-hand side in (2) is due to multiplication by 1, then also the first term of $\varepsilon(\kappa)$ should have the same value. The second term is dictated by the fact that (9) are the eigenfunctions of the Laplace operator, thus the term is $-\kappa^2$ times the coefficient of Δ in $\hat{W}_{sc}$, *i. e.* 1/6 in the sc case. Thus,

$$\varepsilon(\kappa) = 1 - \frac{\kappa^2}{6} + \alpha_2 \kappa^4 \tag{10}$$

where α_2 is a disposable parameter. It is evident from (7) that the parameter is useful only when the polynomials of the third column in (7) are sought out so that (2) is satisfied. Also, since the terms of the 2nd column can arise on the left-hand side of (2) either from the multiplication by a constant or the action of Δ, the disposable coefficients at the functions (9) are useful only for fitting (2) in the polynomials of the 3rd column. The total number of the disposable coefficients is then four (three in (9b) and one in (10)), and since the number of polynomials in the 3rd column in (7) is 11, we can increase the number of

coefficients at these polynomials by 7 supplementary functions which are also of Γ_1 symmetry:

$$\kappa^2 j_2(\kappa R);$$

$$\kappa^2 j_4(\kappa R);$$

$$\kappa^2 j_6(\kappa R);$$

$$\kappa^2\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_6(\kappa R);$$

$$\kappa^2 j_8(\kappa R);$$

$$\kappa^2\left[\left(\frac{X}{R}\right)^4+\left(\frac{Y}{R}\right)^4+\left(\frac{Z}{R}\right)^4\right] j_8(\kappa R);$$

$$\kappa^2\left[\left(\frac{X}{R}\right)^6+\left(\frac{Y}{R}\right)^6+\left(\frac{Z}{R}\right)^6\right] j_8(\kappa R). \tag{11}$$

Denoting the coefficients of the funcions (9b) successively by $c_{4,0}$; $c_{6,0}$ and $c_{8,0}$ and those of (11) by $\bar{c}_{2,1,0}$; $\bar{c}_{4,1,0}$; $\bar{c}_{6,1,0}$; $\bar{c}_{6,2,0}$; $\bar{c}_{8,1,0}$; $\bar{c}_{8,2,0}$ and $\bar{c}_{8,3,0}$ we obtain from (2) the following system of equations:

$$\alpha_2 = (1/120)+(1/15)\bar{c}_{2,1,0}+(2/4725)c_{4,0} \tag{12a}$$

for the term κ^4;

$$-(1/6)\,\alpha_2 = -(1/720)-(1/210)\bar{c}_{2,1,0}-(1/14175)c_{4,0}+(2/567)\bar{c}_{4,1,0} \tag{12b}$$

for the polynomial $\kappa^6 R^2$;

$$\begin{aligned}(1/120)\,\alpha_2-(1/1575)\,\alpha_2 c_{4,0} = (11/181440)+(1/7560)\,\bar{c}_{2,1,0}-\\ -(43/16216200)\,c_{4,0}-1/6237)\,\bar{c}_{4,1,0}+(4/31216185)\,c_{6,0}+\\ +(1/19305)\,\bar{c}_{6,1,0}+(2/135135)\,\bar{c}_{6,2,0}-(4/63996075)\,c_{8,0}\end{aligned} \tag{12c}$$

for the polynomial $\kappa^8 R^4$;

$$\begin{aligned}(1/945)\,\alpha_2 c_{4,0} = (1/68040)+(167/16216200)\,c_{4,0}-(4/18729711)\,c_{6,0}+\\ +(1/36855)\,\bar{c}_{6,2,0}+(4/38397645)\,c_{8,0}\end{aligned} \tag{12d}$$

for the polynomial $\kappa^8(X^4+Y^4+Z^4)$;

$$\begin{aligned}-(1/5040)\,\alpha_2+(1/34650)\,\alpha_2 c_{4,0}+(2/693693)\,\alpha_2 c_{6,0} = -(1/798336)-\\ -(1/498960)\,\bar{c}_{2,1,0}+(1/6486480)\,c_{4,0}+(1/324324)\,\bar{c}_{4,1,0}+\\ +(31/2122700580)\,c_{6,0}-(1/579150)\,\bar{c}_{6,1,0}-(1/2027025)\,\bar{c}_{6,2,0}+\\ +(2/1215925425)\,c_{8,0}+(4/11486475)\,\bar{c}_{8,1,0}+(2/34459425)\,\bar{c}_{8,2,0}\end{aligned} \tag{12e}$$

for the polynomial $\kappa^{10}R^6$;

$$-(1/20790)\,\alpha_2 c_{4,0}-(1/99099)\,\alpha_2\bar{c}_{6,0} = -(1/1496880)-$$
$$-(31/97297200)\,c_{4,0}-(787/12736203480)\,c_{6,0}-(1/1105650)\,\bar{c}_{6,2,0}-$$
$$-(2/3647776275)\,c_{8,0}+(2/7952175)\,\bar{c}_{8,2,0}+(1/6891885)\,\bar{c}_{8,3,0} \tag{12f}$$

for the polynomial $\kappa^{10}R^2(X^4+Y^4+z^4)$;

$$(1/135135)\,\alpha_2 c_{6,0} = -(2/18243225)\,c_{4,0}+(53/1010809800)\,c_{6,0}+$$
$$+(1/6891885)\,\bar{c}_{8,3,0}-(56/18238881375)\,c_{8,0} \tag{12g}$$

for the polynomial $\kappa^{10}(X^6+Y^6+Z^6)$;

$$(1/362880)\,\alpha_2-(1/1801800)\,\alpha_2 c_{4,0}-(1/10405395)\,\alpha_2\bar{c}_{6,0}-$$
$$-(1/191988225)\,\alpha_2 c_{8,0} = (19/1245404160)+(1/51891840)\bar{c}_{2,1,0}-$$
$$-(1/338328900)\,c_{4,0}-(1/29189160)\,\bar{c}_{4,1,0}-(37/65996690760)\,c_{6,0}+$$
$$+(1/39382200)\,\bar{c}_{6,1,0}+(1/137837700)\,\bar{c}_{6,2,0}-(1/15449405400)\,c_{8,0}-$$
$$-(2/218243025)\,\bar{c}_{8,1,0}-(1/654729075)\,\bar{c}_{8,2,0} \tag{12h}$$

for the polynomial $\kappa^{12}R^8$;

$$(1/1081080)\,\alpha_2 c_{4,0}+(1/2972970)\,\alpha_2 c_{6,0}+(2/63996075)\,\alpha_2 c_{8,0} =$$
$$= (1/77837760)+(97/19848628800)\,c_{4,0}+(1039/483975732240)\,c_{6,0}+$$
$$+(1/75184200)\,\bar{c}_{6,2,0}+(1/3979392300)\,c_{8,0}-(1/151091325)\,\bar{c}_{8,2,0}-$$
$$-(1/261891630)\,\bar{c}_{8,3,0} \tag{12i}$$

for the polynomial $\kappa^{12}R^4(X^4+Y^4+Z^4)$;

$$-(1/4054050)\,\alpha_2 c_{6,0}-(4/73841625)\,\alpha_2 c_{8,0} = (2/930404475)\,c_{4,0}-$$
$$-(1723/1037090854800)\,c_{6,0}-(137/328299864750)\,c_{8,0}-$$
$$-(1/261891630)\,\bar{c}_{8,3,0} \tag{12j}$$

for the polynomial $\kappa^{12}R^2(X^6+Y^6+Z^6)$;

$$(1/34459425)\,\alpha_2 c_{8,0} = (1/1240539300)c_{4,0}-(1/21606059475)\,c_{6,0}+$$
$$+(853/3064132071000)\,c_{8,0} \tag{12k}$$

for the polynomial $\kappa^{12}(X^8+Y^8+Z^8)$.

A characteristic point is that the equations (12) are not linear. The algebraic equation to which the system (12) can be reduced is

$$\left(19\alpha_2-\frac{205}{1224}\right)(120\alpha_2-1)\left(19\alpha_2-\frac{145}{1224}\right)\frac{25}{271656}+$$

$$+\left[\frac{1}{799425}-\left(\alpha_2-\frac{853}{88920}\right)\left(\alpha_2-\frac{53}{7480}\right)\frac{741}{392}\right]\left[(120\alpha_2-1)\left(5\alpha_2-\frac{47}{1512}\right)-\frac{2}{567}\right]=0. \tag{12l}$$

Its degree is four; hence, it is equal to the number of functions (9b) plus one. The solutions of (12) are given in Table I, and another characteristic point is that all coefficients at the functions (11) are zero. This occurs for all four solutions of the algebraic equation mentioned.

TABLE I

Solutions of the WS equation for the polynomials of the 3rd column and 4 multiple rows (Eq. (12a)–(12l))

λ	α_2	$c_{4,0}$	$c_{6,0}$	$c_{8,0}$
1	5.540101×10^{-3}	-6.599012	-5.715378×10^{1}	2.273779×10^{1}
2	7.182403×10^{-3}	-2.719073	7.346275×10^{1}	7.994031×10^{1}
3	9.254580×10^{-3}	2.176445	1.015794×10^{1}	-1.308137×10^{2}
4	1.276664×10^{-2}	1.047368×10^{1}	-3.530344×10^{1}	1.094105×10^{2}

Both results given above seem to be general. This means that if we add to column three in (7) the polynomials of X, Y, and Z of order larger than 8 and, at the same time, we add to (9b) and (11) the corresponding functions of order equal to that of the added polynomials, the degree of the algebraic equation established in place of (12l) is once more equal to that of the total number of cubic harmonics introduced into A^{Γ_1}. Also, the coefficients at the functions added to (11) then vanish for all solutions of the algebraic equation. This means that the equations for $c_{l,t,0}$ and α_2 obtained by fitting equation (2) for different polynomials of the 3rd column in (7) are dependent. The set of independent equations for $c_{l,t,0}$ and α_2 can be obtained by choosing from each multiple row in (7) only a number of polynomials equal to that of the cubic harmonics of Γ_1 of order equal to that of the polynomials in a multiple row. The equations fitting (2) for the remaining polynomials of a given multiple row are then satisfied automatically. This makes the calculation of the coefficients self-controlled, as has been checked numerically especially for polynomials in (7) of orders 10 and 12. In the first case only one Laplace eigenfunction, $(KH)^{\Gamma_1}_{10,1}j_{10}$, is added to (9b) and in the second — two functions: $(KH)^{\Gamma_1}_{12,1}j_{12}$ and $(KH)^{\Gamma_1}_{12,1}j_{12}$. In the first case we obtain 5 independent sets of solutions with 5 coefficients in each set, whereas in the second one — 7 sets with 7 coefficients in each set.

Also, the columns of terms can be added to (7). The terms of the p-th column of the extended table (7) can be obtained for example from the 3rd column by multiplying by κ^{2m}, where

$$m=p-3.$$

Equation (2) can be satisfied for the p-th column when: (*i*) the coefficients $c_{4,m}$; $c_{6,m}$, and and $C_{8,m}$ at the functions

$$\kappa^{2(p-3)}(KH)_4^{\Gamma_1} j_4(\kappa R),\ \kappa^{2(p-3)}(KH)_6^{\Gamma_1} j_6(\kappa R) \text{ and } \kappa^{2(p-3)}(KH)_8^{\Gamma_1} j_8(\kappa R), \tag{13}$$

and (*ii*) that at the term

$$\kappa^{2(p-1)} \tag{14}$$

in the expansion of $\varepsilon(\kappa)$, are calculated. (In general, the coefficients at the terms $\kappa^{2m}(KH)_{lt} j_{lm}$ are denoted by $c_{l,t,m}$ [3].) The coefficients by the supplementary functions appropriate for the p-th column

$$\kappa^{2(p-2)} j_2(\kappa R);$$

$$\kappa^{2(p-2)} j_4(\kappa R);$$

$$\kappa^{2(p-2)} j_6(\kappa R);$$

$$\kappa^{2(p-2)} \left[\left(\frac{X}{R}\right)^4 + \left(\frac{Y}{R}\right)^4 + \left(\frac{Z}{R}\right)^4\right] j_6(\kappa R);$$

$$\kappa^{2(p-2)} j_8(\kappa R);$$

$$\kappa^{2(p-2)} \left[\left(\frac{X}{R}\right)^4 + \left(\frac{Y}{R}\right)^4 + \left(\frac{Z}{R}\right)^4\right] j_8(\kappa R);$$

$$\kappa^{2(p-2)} \left[\left(\frac{X}{R}\right)^6 + \left(\frac{Y}{R}\right)^6 + \left(\frac{Z}{R}\right)^6\right] j_8(\kappa R); \tag{15}$$

again vanish. This has been checked numerically for the sc lattice in the case of the 9 columns added to (7). However, the degree of the algebraic equation for the coefficients — or the number of the independent sets of solutions — does not increase when the columns subsequent to the third one are added to (7), because the equations for coefficients at terms (13) and (14) are linear. The coefficients obtained in satisfying (2) for the columns in the extended table (7) with the index n

$$3 \leqslant n < p \tag{16}$$

enter into the equations for the coefficients sought for the p-th column as the known parameters.

2. The property of orthogonality

The functions A^{Γ_1} of equal κ, but different in their combinations of (9b) and (13) due to the plurality of the solutions of the algebraic equation, are denoted henceforth by λ. They are mutually orthogonal in the three-dimensional space of the vector $\boldsymbol{R}$ because $\hat{W}_{sc}$ is a Hermitian operator [3]. This kind of orthogonality has been checked numerically in the case of the extended solutions for the face-centred cubic lattice with $\lambda = 1, 2, 3$ and 4. It is found to be well fulfilled for $\kappa \lesssim 2$ for all λ, and — in the case of some pairs of λ —

for somewhat larger κ [6]. Now, we examine in some detail the orthogonality between two LCAO wave functions of different κ, independently of whether their A^{Γ_1} have the same indices λ or no⁺. We obtain

$$\int\{\sum_i A^{*\Gamma_1,\lambda'}(\boldsymbol{R}_i,\kappa)\varphi^*(\boldsymbol{r}-\boldsymbol{R}_i)\}\{\sum_j A^{\Gamma_1,\lambda''}(\boldsymbol{R}_j,\kappa')\varphi(\boldsymbol{r}-\boldsymbol{R}_j)\}d\tau=$$

$$=\sum_i A^{*\Gamma_1,\lambda'}(\boldsymbol{R}_i,\kappa)A^{\Gamma_1,\lambda''}(\boldsymbol{R}_i,\kappa')\approx$$

$$\approx\frac{1}{v_a}\int A^{*\Gamma_1,\lambda'}(\boldsymbol{R},\kappa)A^{\Gamma_1,\lambda''}(\boldsymbol{R},\kappa')d\Omega. \tag{17}$$

The integration over Ω is extended over the space $\boldsymbol{R}$ of the lattice sites and v_a is the volume of the crystal cell occupied by one atom. The first of the equations in (17) holds due to the orthogonality which — we assume — exists between two atomic orbitals centred on different atomic sites. The replacement of the sum by the integral in the second of the equations is permissible if $A_{1,\lambda}$ do not change too rapidly along the distance between two neighbouring atoms. The final result of (17) is obtained readily if we consider that each of the components of the integral over $\Omega = 4\pi/3R_d^3$ is proportional to:

$$\int_0^{Ra} j_l(\kappa R)j_{l'}(\kappa' R)R^2dR. \tag{18}$$

If j_l and $j_{l'}$ are expanded in series, then the integral (18) calculated at the lower limit vanishes. At the upper limit (R_d very large) the expression (18) becomes

$$\frac{1}{\kappa\kappa'}\int\sin\left(\kappa R-\frac{l}{2}\pi\right)\sin\left(\kappa' R-\frac{l'}{2}\pi\right)dR=$$

$$=-\frac{1}{2\kappa\kappa'}\left(\frac{1}{\kappa+\kappa'}-\frac{1}{\kappa-\kappa'}\right)\sin\left(\kappa R-\frac{l}{2}\pi\right)\cos\left(\kappa' R-\frac{l'}{2}\pi\right)-$$

$$-\frac{1}{2\kappa\kappa'}\left(\frac{1}{\kappa+\kappa'}+\frac{1}{\kappa-\kappa'}\right)\cos\left(\kappa R-\frac{l}{2}\pi\right)\sin\left(\kappa' R-\frac{l'}{2}\pi\right) \tag{19}$$

which vanishes at $R = R_d$ if the boudary conditions of the model

$$\sin\left(\kappa R_d-\frac{l}{2}\pi\right)=0;\quad \sin\left(\kappa' R_d-\frac{l'}{2}\pi\right)=0 \tag{20}$$

(l and l' are even integers or zero) are taken into account. Equation (17) is analogous to the relation

$$\sum_i \exp i(\boldsymbol{k}-\boldsymbol{k}')\boldsymbol{R}_i=0 \tag{17a}$$

of the theory of Bloch which holds for any $\boldsymbol{k}\neq\boldsymbol{k}'$, the sum in (17a) being extended over all lattice sites. It may be noted that (*i*) the property of orthogonality of $(KH)_{l,l'}^{\Gamma_1}$ has not been used in the derivation of (17) and (*ii*) equation (17) is valid for any approximate $A^{1,\lambda}$ of the present scheme.

3. *Density of states per unit range of the energy and band limits*

3.1. Four and five sub-band models

Here we investigate the results corresponding to $(KH)_l^{\Gamma_1} j_l$ with $l = 0, 4, 6$ and 8 ($\lambda = 1, 2, 3$ and 4) and those corresponding to $(KH)_l^{\Gamma_1} j_l$ with $l = 0, 4, 6, 8$ and 10 ($\lambda = 1, 2, 3, 4$ and 5) introduced into A^{Γ_1}. The density of states per unit κ for one sub-band (one of λ's) is [3]:

$$D^{c,\lambda} = \kappa^2 (2\pi^2 [1 + \{\sum_m c_{l,t,m}^{\lambda} \kappa^{2m}\}^2 I_{l,t}])^{-1} \tag{21}$$

where

$$I_{l,t} = (4\pi)^{-1} \int_0^{\pi} d\vartheta \int_0^{2\pi} d\varphi \sin\vartheta [(KH)_{l,t}^{\Gamma_1}]^2$$

and the cell volume v_a has been put equal to 1 due to the primitive translations

$$(1, 0, 0);\ (0, 1, 0) \text{ and } (0, 0, 1) \tag{22}$$

taken into account for the sc lattice. The inflection points of $D^{c,\lambda}$ on the right of which (21) decreases rapidly to zero are given in Table III. The results from the most accurate (most fully expanded) solutions obtained in the present paper (Table II and the corresponding last column in Table III for the 5 sub-bands model) can be compared with the maximum value of $|\boldsymbol{k}|$ for the first Brillouin zone of the sc lattice,

$$|\boldsymbol{k}|_{\max} = \pi\sqrt{3} \cong 5.44, \tag{23}$$

if the primitive translations (22) are taken into account.

The total electron charge

$$Q(\boldsymbol{O}) = \sum_{\lambda} \int_0^{\infty} D^{c,\lambda}(\kappa) d\kappa \tag{24}$$

contributed by the wave functions at site $\boldsymbol{O}$ is presented in Table IV. It is evident that even with the most fully expanded $A^{\Gamma_1 \lambda}$ the results are far from 1, what indicates that the convergence of the sc-solutions — in comparison with the analogous results for the fcc lattice [3] — is the poorest one. The same conclusion stems from a comparison between the density of states per energy unit, $D(\varepsilon)$, in the present scheme with $D(\varepsilon)$ of the theory of Bloch. This is done in Table V for the nearest-neighbour, or tight-binding, approximation.

Bloch's $D(\varepsilon)$ was obtained by dividing 1/8 of the first Brillouin zone for the sc lattice into 512000 equal cubes and calculating the number of cubes whose energies (computed at the cube centers) fall within each of the energy intervals. It can be seen that only solutions of small κ (the energies are close to one of the band limits) can give a satisfactory parallelism with the results of Bloch.

For the most fully expanded solutions attained for the 4 sub-band model about 96.1% of the integral (24) can be obtained if the upper limits in (24) are replaced by:

$$\kappa_m^1 = 9.90;\ \kappa_m^2 = 9.50;\ \kappa_m^3 = 8.90;\ \kappa_m^4 = 8.75. \tag{25}$$

TABLE II

The solutions of the WS equation for coefficients at terms (13) and (14); 5 sub-band model

λ	m	α_2	$c_{4,m}$	$c_{6,m}$	$c_{8,m}$	$c_{10,m}$
	0	5.186937×10^{-3}	-7.433362	-7.747804×10^{1}	4.326579×10^{1}	1.535017×10^{3}
	1	-7.072856×10^{-5}	-1.044231×10^{-3}	-2.673135×10^{-4}	8.103774×10^{-2}	3.177370
	2	5.591330×10^{-7}	-3.120609×10^{-6}	2.898690×10^{-4}	5.623396×10^{-4}	8.311333×10^{-3}
	3	-2.948370×10^{-9}	-1.611861×10^{-7}	1.829871×10^{-6}	7.728306×10^{-6}	4.016504×10^{-5}
1	4	1.125824×10^{-11}	-3.786758×10^{-9}	-3.862963×10^{-9}	1.202347×10^{-7}	7.216623×10^{-7}
	5	-3.293424×10^{-14}	-7.146255×10^{-11}	-3.708196×10^{-10}	1.879504×10^{-9}	1.599097×10^{-8}
	6	7.570453×10^{-17}	-1.244900×10^{-12}	-8.794492×10^{-12}	2.940078×10^{-11}	3.204762×10^{-10}
	7	-1.531892×10^{-19}	-2.091489×10^{-14}	-1.679129×10^{-13}	4.620712×10^{-13}	5.961140×10^{-12}
	8	1.008310×10^{-22}	-3.448255×10^{-16}	-2.953054×10^{-15}	7.305910×10^{-15}	1.060585×10^{-13}
	9	-2.228031×10^{-24}	-5.625601×10^{-18}	-4.994906×10^{-17}	1.161744×10^{-16}	1.836611×10^{-15}
	0	6.978583×10^{-3}	-3.200597	3.849273×10^{1}	2.734583×10^{1}	-1.123064×10^{3}
	1	-1.293384×10^{-4}	2.272487×10^{-4}	-4.497026×10^{-1}	-9.314152×10^{-1}	-1.667393×10^{1}
	2	1.291194×10^{-6}	7.724247×10^{-5}	-1.149467×10^{-2}	-2.556414×10^{-2}	-3.819581×10^{-1}
	3	-9.510125×10^{-9}	2.489132×10^{-6}	-2.396164×10^{-4}	-5.377844×10^{-4}	-7.060931×10^{-3}
	4	3.114295×10^{-11}	6.331587×10^{-8}	-3.292508×10^{-6}	-7.570621×10^{-6}	-7.010122×11^{-5}
2	5	-1.910000×10^{-13}	1.202729×10^{-9}	1.180422×10^{-8}	1.678297×10^{-8}	1.562436×10^{-6}
	6	-6.070200×10^{-15}	1.147350×10^{-11}	2.702432×10^{-9}	5.727041×10^{-9}	1.158335×10^{-7}
	7	2.794175×10^{-16}	-2.793797×10^{-13}	1.076297×10^{-10}	2.328012×10^{-10}	3.933267×10^{-9}
	8	8.231836×10^{-18}	-1.862058×10^{-14}	2.656999×10^{-12}	5.808668×10^{-12}	8.581116×10^{-11}
	9	1.491411×10^{-19}	-5.558623×10^{-16}	3.247247×10^{-14}	7.237795×10^{-14}	7.133772×10^{-13}
	0	7.664925×10^{-3}	-1.579114	-2.648508×10^{2}	-6.508970×10^{2}	-1.248889×10^{4}
	1	-1.652064×10^{-4}	1.269384×10^{-1}	-2.155763×10^{1}	-4.772234×10^{1}	-7.708553×10^{2}
	2	2.119269×10^{-6}	1.279995×10^{-2}	-2.076968	-4.623036	-7.473644×10^{1}
	3	-1.631705×10^{-8}	1.218891×10^{-3}	-1.981926×10^{-1}	-4.410620×10^{-1}	-7.132824
	4	1.068131×10^{-10}	1.159050×10^{-4}	-1.884066×10^{-2}	-4.192621×10^{-2}	-6.779756×10^{-1}
3	5	-3.635570×10^{-13}	1.101127×10^{-5}	-1.789294×10^{-3}	-3.981714×10^{-3}	-6.438326×10^{-2}
	6	-4.405330×10^{-15}	1.045672×10^{-6}	-1.698959×10^{-4}	-3.780696×10^{-4}	-6.113163×10^{-3}
	7	-2.844753×10^{-16}	9.928919×10^{-8}	-1.613147×10^{-5}	-3.589741×10^{-5}	-5.804373×10^{-4}
	8	-8.275112×10^{-18}	9.427526×10^{-9}	-1.531674×10^{-6}	-3.408442×10^{-6}	-5.511219×10^{-5}
	9	-1.489609×10^{-19}	8.951424×10^{-10}	-1.454322×10^{-7}	-3.236309×10^{-7}	-5.232892×10^{-6}
	0	9.854177×10^{-3}	3.592993	1.541906×10^{1}	-1.050127×10^{2}	1.462872×10^{3}
	1	-2.652057×10^{-4}	-1.482242×10^{-3}	5.425807×10^{-2}	8.649435×10^{-2}	7.001450×10^{-1}
	2	3.959736×10^{-6}	6.663146×10^{-5}	5.845627×10^{-4}	2.916951×10^{-3}	3.508885×10^{-2}
	3	-3.730761×10^{-8}	1.096314×10^{-6}	1.031540×10^{-5}	6.517640×10^{-5}	4.954056×10^{-4}
	4	2.422148×10^{-10}	9.691945×10^{-9}	2.024653×10^{-7}	1.255320×10^{-6}	4.928074×10^{-6}
4	5	-1.145908×10^{-12}	-5.499055×10^{-11}	4.166566×10^{-9}	2.285658×10^{-8}	1.952895×10^{-8}
	6	4.188990×10^{-15}	-5.204501×10^{-12}	8.716359×10^{-11}	4.116884×10^{-10}	7.246016×10^{-10}
	7	-1.121186×10^{-17}	-1.647350×10^{-13}	1.819669×10^{-12}	7.514517×10^{-12}	-2.945592×10^{-11}
	8	4.011161×10^{-20}	-4.126568×10^{-15}	3.764371×10^{-14}	1.404341×10^{-13}	-7.854059×10^{-13}
	9	2.003783×10^{-22}	-9.333125×10^{-17}	7.712876×10^{-16}	2.688746×10^{-15}	-1.826217×10^{-14}
	0	1.294823×10^{-2}	1.090269×10^{1}	-4.208868×10^{1}	1.288361×10^{2}	-8.879524×10^{2}
	1	-4.163914×10^{-4}	-2.857761×10^{-4}	-3.775417×10^{-3}	-3.047357×10^{-2}	3.231007×10^{-1}

TABLE II (continued)

λ	m	α_2	$c_{4,m}$	$c_{6,m}$	$c_{8,m}$	$c_{10,m}$
	2	7.198652×10^{-6}	4.594992×10^{-5}	-5.165406×10^{-4}	2.386912×10^{-3}	-3.025683×10^{-2}
	3	-7.756226×10^{-8}	1.109925×10^{-6}	-1.160259×10^{-5}	5.481402×10^{-5}	-6.780221×10^{-4}
	4	5.707318×10^{-10}	1.828869×10^{-8}	-1.947043×10^{-7}	9.251464×10^{-7}	-1.158548×10^{-5}
5	5	-3.047659×10^{-12}	2.404703×10^{-10}	-2.774506×10^{-9}	1.348644×10^{-8}	-1.763393×10^{-7}
	6	1.237436×10^{-14}	2.512188×10^{-12}	-3.466748×10^{-11}	1.776236×10^{-10}	-2.500743×10^{-9}
	7	-3.922870×10^{-17}	1.663848×10^{-14}	-3.728520×10^{-13}	2.140812×10^{-12}	-3.360558×10^{-11}
	8	1.023023×10^{-19}	-8.620014×10^{-17}	-3.071268×10^{-15}	2.342008×10^{-14}	-4.297265×10^{-13}
	9	-2.016202×10^{-22}	-6.132402×10^{-18}	-6.957579×10^{-18}	2.233475×10^{-16}	-5.201556×10^{-15}

TABLE III

The inflection points κ_i^λ of $D^{c,\lambda}(\kappa)$ for the 4 sub-band and 5 sub-band models

4 sub-band model

λ \ m	1	2	3	4	5	6	7	8	9
1	52	27	15	12	11	10.4	10	9.7	9.5
2	78	26	17	13	11	10.2	10	9.6	9.1
3	67	23	14	12	10	9.7	9.6	9.1	8.7
4	51	24	14	11	10	9.9	11	10	9.8
	5 sub-band model								
1	52	24	17	13.7	11.8	10.8	10.1	9.7	9.4
2	13.4	7.8	6.8	6.5	6.6	7.9	6.9	6.6	6.5
3	6.0	3.5	3.0	2.9	2.8	2.8	2.9	2.9	2.9
4	48.2	16.0	11.0	9.9	9.2	8.7	8.3	8.1	7.9
5	108	18.0	12.0	10.2	9.5	9.1	9.0	8.8	8.7

TABLE IV

Total electron charge $\mathbf{Q}(O)$ contributed by the wave functions at site O

Model	m								
	1	2	3	4	5	6	7	8	9
4 sub--bands	4.23×10^{3}	3.13×10^{2}	7.09×10^{1}	3.66×10^{1}	2.53×10^{1}	2.00×10^{1}	1.69×10^{1}	1.50×10^{1}	1.37×10^{1}
5 sub--bands	7.40×10^{3}	9.15×10^{1}	2.39×10^{1}	1.47×10^{1}	1.15×10^{1}	1.13×10^{1}	9.67	8.70	8.17

TABLE V

The density of states $D(\varepsilon)$ per energy unit for the 4 sub-band model in comparison with Bloch

$\Delta\varepsilon$	λ				Total $D(\varepsilon)$	Bloch $D(\varepsilon)$
	1	2	3	4		
1.033 — 1.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000 — 0.967	0.012	0.011	0.015	0.008	0.046	0.046
0.967 — 0.933	0.023	0.021	0.028	0.014	0.086	0.086
0.933 — 0.900	0.030	0.027	0.038	0.019	0.114	0.115
0.900 — 0.867	0.036	0.034	0.047	0.024	0.141	0.139
0.867 — 0.833	0.041	0.038	0.052	0.029	0.160	0.163
0.833 — 0.800	0.046	0.044	0.065	0.033	0.188	0.185
0.800 — 0.767	0.052	0.048	0.067	0.038	0.205	0.207
0.767 — 0.733	0.058	0.053	0.078	8.032	8.221	0.231
0.733 — 0.700	0.062	0.057	0.085	4.177	4.381	0.254
−0.700 — −0.733	4.681	0.000	0.000	0.000	4.681	0.254
−0.733 — −0.767	9.066	0.000	0.000	0.000	9.066	0.231
−0.767 — −0.800	2.087	0.000	0.000	0.000	2.087	0.207
−0.800 — −0.833	0.000	0.000	0.000	0.000	0.000	0.185
−0.833 — −0.867	0.000	0.000	0.000	0.000	0.000	0.163
−0.867 — −0.900	0.000	0.000	0.000	0.000	0.000	0.139
−0.900 — −0.933	0.000	0.000	0.000	0.000	0.000	0.115
−0.933 — −0.967	0.000	0.000	0.000	0.000	0.000	0.086
−0.967 — −1.000	0.000	0.000	0.000	0.000	0.000	0.046
−1.000 — −1.033	0.000	0.000	0.000	0.000	0.000	0.000

This gives one extreme value for the energy equal to 1 and attained by all ε^λ at $\kappa = 0$; the other value is $\varepsilon^1 \approx -0.77$ obtained at $\kappa = 5.3$. Thus the band width is *ca* 90% of that of Bloch[2], because the Bloch energy corresponding to [3] and (22) is

$$\varepsilon(k_x, k_y, k_z) = \frac{E - E^0 - \gamma}{q\beta} = \frac{1}{3}(\cos k_x + \cos k_y + \cos k_z). \tag{26}$$

The extrema of (26) are: (*i*) $\varepsilon = 1$ attained for $k_x = k_y = k_z = 0$ and (*ii*) $\varepsilon = -1$ attained for $k_x = \pi$, $k_y = k_z = 0$ (or for $k_x = k_y$ and k_z obtained by a cyclic interchange of the subscripts in the last expressions).

Tables VI and VII give a comparison between the nearly-free electron

$$D(\varepsilon) = \frac{dn}{d\kappa} \cdot \frac{d\kappa}{dE} [A^{\Gamma_1,\lambda}(\boldsymbol{O}, \kappa)]^2 = \sum_\lambda \kappa^{-1} D^{c,\lambda}(\kappa) \tag{27}$$

[2] In the case of the 5 sub-band model the extreme values of energy are respectively 1, attained for all ε^λ, and $\varepsilon^1 = -0.86$.

TABLE VI

The density of states, $(2\pi^2)\,D(\varepsilon)$, per energy unit, for the 4 sub-band model for the nearly-free electron approximation in comparison with Bloch; ε is below the critical point of Bloch's theory

κ	Contributions from different sub-bands for λ				Total $(2\pi^2)\,D(\varepsilon)$	Bloch $(2\pi^2)\,D(\varepsilon)$
	1	2	3	4		
0.30	8.02224635×10^{-2}	7.21884391×10^{-2}	9.88329523×10^{-2}	4.87561467×10^{-2}	3.00000001×10^{-1}	0.30000000
0.60	1.60388058×10^{-1}	1.44410003×10^{-1}	1.97668009×10^{-1}	9.75339336×10^{-2}	6.00000001×10^{-1}	0.60000000
0.90	2.40440321×10^{-1}	2.16697998×10^{-1}	2.96506913×10^{-1}	1.46354770×10^{-1}	9.00000000×10^{-1}	0.90000000
1.20	3.20323644×10^{-1}	2.89086099×10^{-1}	3.95350679×10^{-1}	1.95239577×10^{-1}	1.20000000	1.20000000
1.50	3.99983813×10^{-1}	3.61608551×10^{-1}	4.94199180×10^{-1}	2.44208448×10^{-1}	1.49999999	1.50000000
1.80	4.79368673×10^{-1}	4.34300395×10^{-1}	5.93050718×10^{-1}	2.93280198×10^{-1}	1.79999998	1.80000000
2.10	5.58429021×10^{-1}	5.07197730×10^{-1}	6.91901499×10^{-1}	3.42471730×10^{-1}	2.09999998	2.10000000
2.40	6.37119792×10^{-1}	5.80338050×10^{-1}	7.90744988×10^{-1}	3.91797139×10^{-1}	2.39999996	2.40000000
2.70	7.15401690×10^{-1}	6.53760700×10^{-1}	8.89571114×10^{-1}	4.41266456×10^{-1}	2.69999995	2.70000000
3.00	7.93243485×10^{-1}	7.27507556×10^{-1}	9.88365052×10^{-1}	4.90883849×10^{-1}	2.99999993	3.00000000

TABLE VII

The density of states, $(2\pi^2)\ D(\varepsilon)$, per energy unit, for the 5 sub-band model for the nearly-free electron approximation in comparison with Bloch; ε is below the critical point of Bloch's theory

κ	Contributions from different sub-bands for λ					Total $(2\pi^2)\ D(\varepsilon)$	Bloch $(2\pi^2)\ D(\varepsilon)$
	1	2	3	4	5		
0.30	4.82399864×10^{-2}	1.22088410×10^{-1}	2.25162056×10^{-3}	8.70535749×10^{-2}	4.03664075×10^{-2}	2.99999999×10^{-1}	0.30000000
0.60	9.64601787×10^{-2}	2.44352478×10^{-1}	4.33251004×10^{-3}	1.74118937×10^{-1}	8.07358942×10^{-2}	5.99999996×10^{-1}	0.60000000
0.90	1.44640798×10^{-1}	3.66965793×10^{-1}	6.07457355×10^{-3}	2.61208022×10^{-1}	1.21110809×10^{-1}	8.99999993×10^{-1}	0.90000000
1.20	1.92762091×10^{-1}	4.90096034×10^{-1}	7.31676962×10^{-3}	3.48333115×10^{-1}	1.61491977×10^{-1}	1.19999998	1.20000000
1.50	2.40804340×10^{-1}	6.13897081×10^{-1}	7.91362886×10^{-3}	4.35507162×10^{-1}	2.01877771×10^{-1}	1.49999998	1.50000000
1.80	2.88747846×10^{-1}	7.38493506×10^{-1}	7.75149641×10^{-3}	5.22744276×10^{-1}	2.42262952×10^{-1}	1.80000007	1.80000000
2.10	3.36572905×10^{-1}	8.63951689×10^{-1}	6.77954650×10^{-3}	6.10060565×10^{-1}	2.82637172×10^{-1}	2.10000187	2.10000000
2.40	3.84259732×10^{-1}	9.90228090×10^{-1}	5.07500663×10^{-3}	6.97475489×10^{-1}	3.22983010×10^{-1}	2.40002131	2.40000000
2.70	4.31788347×10^{-1}	1.11707938	2.98143680×10^{-3}	7.85014063×10^{-1}	3.63273275×10^{-1}	2.70013650	2.70000000
3.00	4.79138320×10^{-1}	1.24391176	1.20493456×10^{-3}	8.72710468×10^{-1}	4.03467343×10^{-1}	3.00043282	3.00000000

of the present method with the same $D(\varepsilon)$ of Bloch in the interval of $|\boldsymbol{k}|$ between zero and the value for which the Fermi surface touches the boundary of the first Brillouin zone, *i.e.*

$$|\boldsymbol{k}| = \kappa = \pi. \tag{28}$$

In this interval $D(\varepsilon)$ of Bloch is exactly

$$D(\varepsilon) = |\boldsymbol{k}|/2\pi^2 \tag{29}$$

if $\hbar$ and m_e are put equal to 1. The comparison has been limited only to the interval determined by (28) because for $|\boldsymbol{k}| = \pi$.

Bloch's $D(\varepsilon)$ decreases sharply to zero and can be obtained only in an approximate way, analogous to that applied for Bloch's $D(\varepsilon)$ in the tight-binding case; also $D(\varepsilon)$ of (27) are inaccurate in the interval of κ larger than that corresponding to (28) in view of the inaccuracy of $D(\varepsilon)$ obtained numerically for large κ.

3.2. Seven sub-band model

At the next step, we can introduce cubic harmonics with $l = 12$ to the expansion, in addition to those with $l = 0$, 4, 6, 8 and 10. Then we have two distinct components:

$$(KH)^{\Gamma_1}_{12,1} = \frac{x^4y^4z^4}{R^{12}} + \left(\frac{6}{115}\right)(KH)^{\Gamma_1}_{10} - \left(\frac{1}{2\cdot 7\cdot 19}\right)(KH)^{\Gamma_1}_{8} -$$

$$- \left(\frac{18}{5\cdot 17\cdot 19}\right)(KH)^{\Gamma_1}_{6} + \left(\frac{3}{11\cdot 13\cdot 17}\right)(KH)^{\Gamma_1}_{4} - \frac{1}{5\cdot 7\cdot 11\cdot 13}; \tag{30a}$$

$$(KH)^{\Gamma_1}_{12,2} = \left(\frac{x}{R}\right)^{12} + \left(\frac{y}{R}\right)^{12} + \left(\frac{z}{R}\right)^{12} - \left(\frac{66}{23}\right)(KH)^{\Gamma_1}_{10} - \left(\frac{11\cdot 45}{7\cdot 19}\right)(KH)^{\Gamma_1}_{8} -$$

$$- \left(\frac{33\cdot 28}{17\cdot 19}\right)(KH)^{\Gamma_1}_{6} - \left(\frac{5\cdot 7\cdot 9}{13\cdot 17}\right)(KH)^{\Gamma_1}_{4} - \frac{3}{13}; \tag{30b}$$

where $(KH)^{\Gamma_1}_6$ is that of the present calculations (see the footnote in Section 1). Let us note that a printing error in [5] in the coefficient at $(KH)^{\Gamma_1}_{10}$ in $(KH)^{\Gamma_1}_{12,2}$ has been revealed.

The respective normalization coefficients of the functions (30a) and (30b) to the value 4π are:

$$(4\pi I_{12,1})^{-\frac{1}{2}} = \left(\frac{11}{41\cdot 4\pi}\right)^{\frac{1}{2}} \frac{3\cdot 7\cdot 13\cdot 17\cdot 19\cdot 23}{32}; \tag{31a}$$

$$(4\pi I_{12,2})^{-\frac{1}{2}} = \frac{25}{32}\left(\frac{7\cdot 13\cdot 17\cdot 19\cdot 23\cdot 41}{6\cdot 4\pi}\right)^{\frac{1}{2}}. \tag{31b}$$

The introduction of $(KH)^{\Gamma_1}_{12,1}$ and $(KH)^{\Gamma_1}_{12,2}$ into A provides a 7 sub-band model. The coefficients at the components $(KH)^{\Gamma_1}_{l,t} j_l$ and α_2 have been calculated only for the case of the largest power m equal to zero (Table VIII). All coefficients at the supplementary functions of the type given in (11) vanish.

TABLE VIII

Solutions of the WS equation for the polynomials of the 3rd column and 7 multiple rows of the extended Eq. (7)

λ	α_2	$c_{4,0}$	$c_{6,0}$	$c_{8,0}$	$c_{10,0}$	$c_{12,1,0}$	$c_{12,2,0}$
1	5.066119×10^{-3}	-7.718795	-8.594874×10^{1}	4.855122×10^{1}	2.217754×10^{3}	2.467121×10^{4}	-1.108000×10^{2}
2	6.254330×10^{-3}	-4.911646	-2.096638	2.812513×10^{1}	-1.658631×10^{3}	-4.718627×10^{4}	-3.581519×10^{2}
3	7.067913×10^{-3}	-2.989556	1.203396×10^{2}	1.865242×10^{2}	8.656854×10^{2}	3.733751×10^{4}	-1.869050×10^{3}
4	7.922995×10^{-3}	-9.694252×10^{-1}	1.477403×10^{1}	-9.298312×10^{1}	-1.133727×10^{3}	3.165782×10^{4}	1.056141×10^{3}
5	9.115256×10^{-3}	1.847293	6.241788×10^{1}	-2.469435×10^{1}	4.018824×10^{3}	-5.318758×10^{4}	4.300075×10^{3}
6	1.093808×10^{-2}	6.153710	-5.835482	-7.765202×10^{1}	1.019049×10^{3}	-1.077729×10^{4}	-2.225769×10^{3}
7	1.324578×10^{-2}	1.160566×10^{1}	-4.740678×10^{1}	1.759797×10^{2}	-1.315779×10^{3}	9.521041×10^{3}	1.573565×10^{3}

Even a model not greatly expanded in powers of κ should give a fairly accurate description of the density of states at small κ. In the case of the 7 sub-band model we check this for the nearly-free electron approximation at the limiting value of $\kappa = 0$. Then we have from all sub-bands:

$$\lim_{\kappa \to 0} \kappa^{-2} \sum_{\lambda=1}^{\lambda=7} D^{c,\lambda}(\kappa) = (2\pi)^{-1}(0.118201440 + 0.203462699 + 0.072243136 +$$

$$+ 0.260624669 + 0.056404756 + 0.197841990 + 0.091221182) =$$

$$= 0.999999872(2\pi)^{-1}. \tag{32}$$

Hence, the nearly-free electron density of states per unit range of energy at very small κ is

$$\kappa^{-1} \sum_{\lambda} D^{c,\lambda} = 0.999999872(2\pi)^{-1}\kappa \approx (2\pi)^{-1}\kappa, \tag{33}$$

as might be expected on the basis of the almost-free electron solutions of Bloch which can be considered as exact in the energy interval below the critical point (see equation (29) and the end of Section 3.2; ; *cf.* also [3]).

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