

The Empty Lattice Test of the Cellular Method in Solids*

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The cellular method of constructing wave functions for electrons in crystals developed principally by Wigner and Seitz and Slater is tested by applying it to an artificial crystal in which the potential is constant. Knowledge of the exact solutions for this case, plane waves, shows that the cellular method is quite accurate in the first Brillouin zone but may be in error by a factor of two in the second. Hence calculations of occupied levels in Li and Na are probably quite good; for Cu, Ca, diamond, LiF, and NaCl the errors will be larger. Calculations of excited states are likely to be very much in error. The accuracy of the cellular method is shown to improve very slowly with increasing number of continuity conditions.

I. INTRODUCTION

THE cellular method of constructing lattice functions, developed principally by Wigner and Seitz¹ and Slater² has now been applied to a large number of cases. However, no critical evaluation of the rigor of the method has as yet been presented. A new exact method has been developed by Slater,³ but since this has not been applied to any problem, a comparison with the results of the cellular method is not possible.

In order to obtain lattice functions by the cellular method the lattice is partitioned into Wigner-Seitz cells within which the potential is taken to have spherical symmetry. The lattice function in one cell is then expanded in spherical harmonics times solutions of the radial part of the wave equation. The wave function in other cells is obtained by translation and multiplication by $\exp(2\pi i \mathbf{k} \cdot \mathbf{R})$ where \mathbf{R} is the translation vector and \mathbf{k} is a vector analogous to the momentum for a plane wave divided by h . By the cellular method one obtains a functional relationship between \mathbf{k} and the energy $E(\mathbf{k})$ of the lattice function.

There is only one obvious exactly soluble case to which the cellular method can be applied. This is the trivial case of the "empty lattice"—the spherically symmetrical potential becoming a constant. The radial functions needed in the

cellular method are known and the exact solutions are those for the free electron. Hence it is possible to compare cellular solutions with exact solutions and thus gain an estimate of the accuracy of the method.

II. EMPTY LATTICE TEST FOR THE FACE-CENTERED LATTICE

The Schrödinger equation for one electron when expressed in atomic units is

$$\nabla^2 \psi + (E - V)\psi = 0. \quad (1)$$

For the empty lattice it becomes

$$\nabla^2 \psi + E\psi = 0 \quad (2)$$

and has solutions

$$\psi = \exp 2\pi i \mathbf{k} \cdot \mathbf{r} \quad (3)$$

with energies

$$E = 4\pi^2 k^2. \quad (4)$$

Now suppose that an artificial face-centered lattice is inserted in space with lattice vectors $0 \pm \frac{1}{2} \pm \frac{1}{2}$, etc. The cell appropriate to this lattice is rhombic duodecahedron bounded by planes bisecting the above set of vectors. The wave equation inside the cell may be separated in spherical coordinates and has solutions of the form

$$\psi_l = S_{ml}(\theta, \varphi) f_e(r), \quad (5)$$

where S_{ml} is a tesseral harmonic of degree l and $f_l(r)$ satisfies the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} f(r) \right) + \left[E - \frac{l(l+1)}{r^2} \right] f(r) = 0. \quad (6)$$

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¹ E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933) and **46**, 509 (1934).

² J. C. Slater, Phys. Rev. **45**, 794 (1934).

³ J. C. Slater, Phys. Rev. **51**, 846 (1937).

Since the solutions of this equation are the well-known functions⁴

$$j_l(E^{\frac{1}{2}}r) = \left(\frac{\pi}{2E^{\frac{1}{2}}r}\right)^{\frac{1}{2}} J_{l+\frac{1}{2}}(E^{\frac{1}{2}}r), \quad (7)$$

where $J_n(r)$ represents a Bessel function, the procedure of setting up cellular lattice functions may be carried out. The expressions arising from this procedure involve the ratios $s'/s = \sigma$, $p'/p = \pi$, $d'/d = \delta$, $f'/f = \varphi^5$ where s , p , d , and f are the radial wave functions for $l=0, 1, 2$, and 3 and s' , p' , d' and f' are their derivatives in respect to increasing r . These quantities are evaluated at the midpoints of the intercellular boundaries, $r=r_0=2^{\frac{1}{2}}/4$. Hence the ratios take the form

$$\sigma = s'/s = E^{\frac{1}{2}}j_0'(E^{\frac{1}{2}}r_0)/j_0(E^{\frac{1}{2}}r_0). \quad (8)$$

The cellular method supposes that the lattice wave functions are expressed in the form $\exp(2\pi i \mathbf{k} \cdot \mathbf{x}) \varphi(\mathbf{x})$ where $\varphi(\mathbf{x})$ is a periodic function of position in the lattice; the energy $E(\mathbf{k})$ of the wave functions is calculated as a function of \mathbf{k} . It is most convenient to suppose that \mathbf{k} is in the first Brillouin zone of k space. The energy and wave function are then multivalued functions of \mathbf{k} . The corresponding exact plane wave solutions will be

$$\psi_{K, k}(x) = \exp(2\pi i \mathbf{k} \cdot \mathbf{r}) \exp(2\pi i \mathbf{K} \cdot \mathbf{r}), \quad (9)$$

$$E_K(\mathbf{k}) = 4\pi^2(\mathbf{K} + \mathbf{k})^2, \quad (10)$$

TABLE I. Classification for the six lowest branches of the $E_K(\mathbf{k})$ curves.

Γ_1	
$E_{000}(u) = 4\pi^2 3u^2$	$\psi = \psi_{000}$
$E_{-1-1-1}(u) = 4\pi^2 3(u-1)^2$	$\psi = \psi_{-1-1-1}$
$E_{111}(u) = 4\pi^2 3(u+1)^2$	$\psi = \psi_{111}$
$E_{1-1-1}(u) = 4\pi^2 [2(u-1)^2 + (u+1)^2]$	$\psi = \psi_{1-1-1} + \psi_{-11-1} + \psi_{-1-11}$
$E_{-111}(u) = 4\pi^2 [2(u+1)^2 + (u-1)^2]$	$\psi = \psi_{-111} + \psi_{-1-11} + \psi_{11-1}$
$E_{-200}(u) = 4\pi^2 [2u^2 + (u-2)^2]$	$\psi = \psi_{-200} + \psi_{0-20} + \psi_{00-2}$
Γ_2	
has no representations for energies as low as those considered here.	
Γ_3	
$E_{1-1-1}(u) = 4\pi^2 [2(u-1)^2 + (u+1)^2]$	$\psi = \psi_{1-1-1} + \omega_1 \psi_{-11-1} + \omega_2 \psi_{-1-11}$ and $\psi = \psi_{1-1-1} + \omega_2 \psi_{-11-1} + \omega_1 \psi_{-1-11}$
$E_{-111}(u) = 4\pi^2 [2(u+1)^2 + (u-1)^2]$	$\psi = \psi_{-111} + \omega_1 \psi_{1-11} + \omega_2 \psi_{11-1}$ and $\psi = \psi_{-111} + \omega_2 \psi_{1-11} + \omega_1 \psi_{11-1}$
$E_{-200}(u) = 4\pi^2 [2u^2 + (u-2)^2]$	$\psi = \psi_{-200} + \omega_1 \psi_{0-20} + \omega_2 \psi_{00-2}$ and $\psi = \psi_{-200} + \omega_2 \psi_{0-20} + \omega_1 \psi_{00-2}$

⁴ Excellent tables of these functions are given in *Vibration and Sound* by P. M. Morse, to whom the writer is indebted for their use in advance of their publication.

⁵ The notation used in this paper, especially in regard to the face-centered solutions, is that of W. Shockley, *Phys. Rev.* **51**, 130 (1937). π means $3.14 \dots$ when it multiplies \mathbf{k} or its components.

where \mathbf{K} is a vector of the reciprocal lattice and is a sum of vectors of the form $\pm 1 \pm 1 \pm 1$.

The test described in this work is carried out by calculating $E(\mathbf{k})$ from the solutions worked out by Krutter⁶ and comparing them with the exact $E_K(\mathbf{k})$. This comparison is complicated by the fact that both sets of functions are multivalued. For principal crystallographic directions, however, segregation into noncombining types is made possible by symmetry considerations. When \mathbf{k} lies in the 111 direction, whose symmetry is C_{3v} , it is possible to group the wave functions into three different types:⁷ Γ_1 , functions which are unaltered by the symmetry operations of the three fold rotation and reflection axis in the 111 direction; Γ_2 , functions which are unaltered by rotation but change sign on reflection; Γ_3 , functions occurring in pairs which transform as do $e^{+i\varphi}$ and $e^{-i\varphi}$ where φ is the angle measured around 111 as an axis. The classification for the six lowest branches of the $E_K(\mathbf{k})$ curves is given in Table I. For brevity only one component of $\mathbf{k}=u$, u , u is given; $\psi_{K, k}(\mathbf{r}) = \psi_K$, and $\omega_1 = e^{2\pi i/3}$, $\omega_2 = \omega_1^2$.

The classification of the results of the cellular method is given in Table II. The notation is that of reference 5. The energy was computed as a function of u from these relationships. The work is slightly simplified by the fact that all the expressions are homogeneous of zero degree in the quantities σ , π , etc., hence no error is made by omitting the factor $E^{\frac{1}{2}}$ which occurs in Eq. (8).

The results of the work are shown in Fig. 1. For energies below 30 units on this scale, we see

TABLE II. Classification of the results of the cellular method.

	Γ_1
111 _a	$\tan^2 \pi u + 2\sigma \delta / \pi(\sigma + \delta) = 0$
	Γ_2
111 _f	u arbitrary for $\varphi = \infty$.
	(No solutions in the energy range considered.)
	Γ_3
111 _b and 111 _c	$\tan^2 \pi u + 4\delta / (\pi + 3\varphi) = 0$
111 _d and 111 _e	u arbitrary for $\delta = 0$

⁶ H. M. Krutter, *Phys. Rev.* **48**, 664 (1935).

⁷ Group theoretical classifications into symmetry types for many crystallographic directions have been given by Bouckaert, Smoluchowski, and Wigner, *Phys. Rev.* **50**, 63 (1936). The character scheme for this case is given in their Table III.

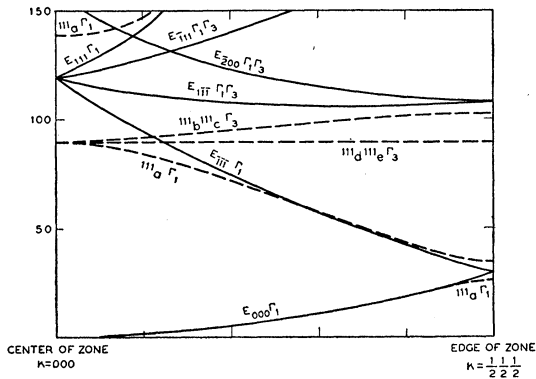


FIG. 1. Comparison of cellular and exact solutions for the face-centered lattice, 111 direction. Cellular solutions, dashed lines; exact solutions, solid lines. Solutions of the same symmetry type should be compared.

that both the cellular method and the exact solution give only one energy value and that the two agree extremely well. The agreement is still fairly satisfactory up to about 80 units. If the method were exact we should find that the Γ_1 curves for the cellular method would coincide with the Γ_1 curves of the exact solution and a similar situation would hold true for the Γ_2 curves. It is readily seen, however, that the results of the cellular method become notably faulty above about 90 units.

For other directions in the face-centered lattice similar results are obtained, the agreement for the lowest curve being nearly but not quite as good.

III. EMPTY LATTICE TEST FOR THE BODY-CENTERED LATTICE

A similar process can be carried out for a body-centered lattice. For this lattice the translations are composed of vectors of the form $\pm\frac{1}{2}\pm\frac{1}{2}\pm\frac{1}{2}$ with corresponding reciprocal vectors $0\pm 1\pm 1$. The cell is a truncated octahedron and the midpoints of the faces between nearest neighbors are at $\pm\frac{1}{4}\pm\frac{1}{4}\pm\frac{1}{4}$. From these we find $r_0 = 3^{1/2}/4$, in terms of which σ , π , etc., are found by equation 8. Taking the 100 direction for test purposes, we classify our wave functions according to the symmetry C_{4v} of this direction. There are five classifications:⁸ Γ_1 , single functions unaltered by the symmetry operations; Γ_2 , single functions which change sign when rotated 90° or when

reflected in the 011 or $01\bar{1}$ planes; Γ_3 , single functions which change sign when rotated 90° or reflected in the 010 or 001 planes; Γ_4 , single functions which change sign when reflected in either 010, 001, 011, or $01\bar{1}$ planes; Γ_4 , pairs of functions which transform as do $e^{i\varphi}$ and $e^{-i\varphi}$. With this classification and with $k = u00$ the energy curves of Fig. 2 and Table III were constructed. All energies less than 150 units are included.

Not all of the symmetry types are represented in the cellular solutions² (Table IV). We see that Γ_2 , which gives several energy contours below 150 units, is not represented in the cellular method. Due to the complexity of the curves the symmetry types are compared on separate diagrams.

The curves for the 111 direction of the face-centered lattice and the 100 direction of the body-centered lattice are quite typical. For other directions the agreement is similar on the whole. Being worse in some respects, better in others.

IV. REASON FOR THE DISCREPANCIES

The reason for the good agreement in the first zone and poor agreement in the higher zones is easily understood by considering the expansion of a plane wave in spherical harmonics. This expansion involves zonal harmonics of all orders; however, if we are interested in the expansion within only a fraction of a wave-length about a certain point only the first few terms are large. This is the situation met with in the first zone for which the radius of the cell corresponds to less than $\frac{1}{4}$ wave-length, and the first three or four harmonics give a good expansion. However, the number of terms needed increases rapidly when the region of expansion is doubled—center of the second zone—and not enough harmonics are present in the cellular formulation. Hence the agreement becomes bad.

V. APPLICATION OF THE RESULTS

It is natural to apply these results to calculations previously made with the cellular method with a view to estimating the error arising there. In order to do this it is necessary to compare lattices of the same size. From considerations of

⁸ Reference 7, Table II.

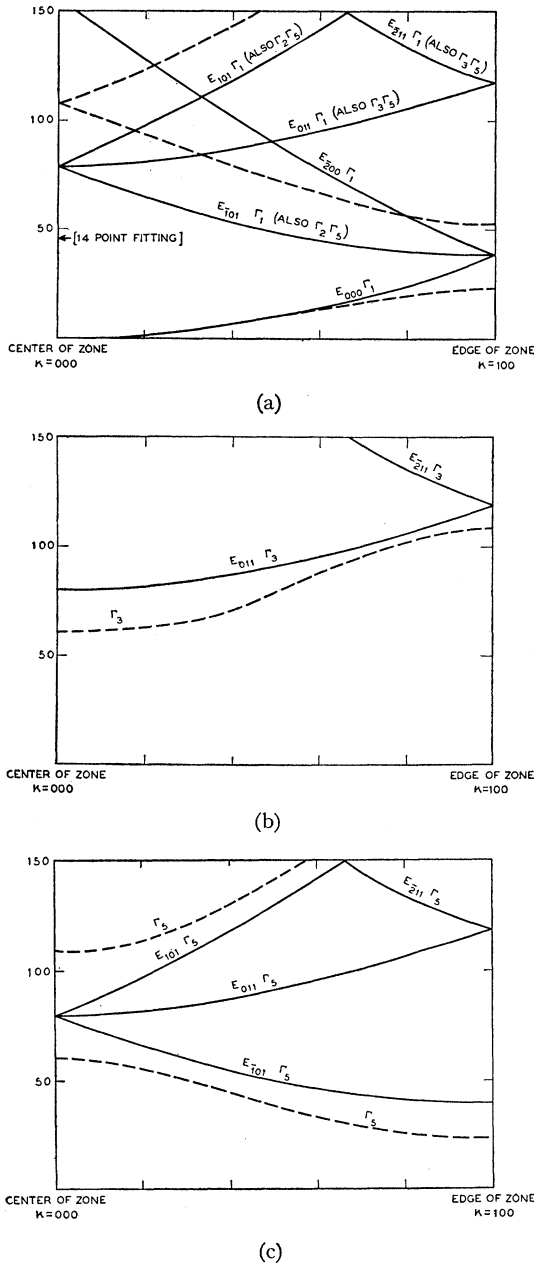


FIG. 2. Comparison of cellular and exact solutions for the body-centered lattice 100 direction. (a), Γ_1 type cellular solution, dashed line. All exact solutions, solid lines, with energies less than 150 units are shown. An energy curve will originate at point marked "14 point fitting" if continuity conditions are introduced on cubic faces. (b), Γ_3 type. Cellular solution, dashed line, exact, solid line. (c), Γ_5 type. Cellular solution, dashed line; exact, solid line.

Eqs. (8) and (10) it is readily apparent that with a lattice constant of "a" rather than unity, the shape of the curves in figures will be unaltered

but the energy scale will be modified by a factor $1/a^2$. It is, however, more convenient to reduce the results for the actual lattice to those of the unit lattice by multiplying by a^2 .

A diagram indicating the error of the cellular approximation was constructed as follows: For various different computed values of the energy, the corresponding correct energies were found; of these the two lying farthest above and below the computed energy and the two lying nearest the computed energy were chosen. These values were taken as liberal and conservative estimates of the error in the method, errors greater than those of the liberal curve or less than those of the conservative curve being regarded as unlikely.

The results of the above analysis are shown in Fig. 3. The energy distribution for some of the crystals for which calculations have been made are also shown reduced to the same scale. Energy values normally occupied are shaded, and in two cases energy gaps between filled and empty bands are shown. It is seen that calculations for the alkali metals,⁹ for which the first zone is only partly filled should have quite small

TABLE III. Representations for the body-centered lattice with the wave functions classified according to the symmetry C_{4v} of the 100 direction. Energies less than 150 units are included.

$E_{000}(u) = 4\pi^2 u^2$	Γ_1	$\psi = \psi_{000}$
$E_{-200}(u) = 4\pi^2 (u-2)^2$		$\psi = \psi_{200}$
$E_{-101}(u) = 4\pi^2 \{(u-1)^2 + 1\}$		$\psi = \psi_{-101} + \psi_{-110} + \psi_{-10-1} + \psi_{-1-10}$
$E_{101}(u) = 4\pi^2 \{(u+1)^2 + 1\}$		$\psi = \psi_{101} + \psi_{110} + \psi_{10-1} + \psi_{1-10}$
$E_{011}(u) = 4\pi^2 (u^2 + 2)$		$\psi = \psi_{011} + \psi_{01-1} + \psi_{0-1-1} + \psi_{0-11}$
$E_{-211}(u) = 4\pi^2 \{(u-2)^2 + 2\}$		$\psi = \psi_{-211} + \psi_{-21-1} + \psi_{-2-1-1} + \psi_{-2-11}$
	Γ_2	
$E_{-101}(u) = 4\pi^2 \{(u-1)^2 + 1\}$		$\psi = \psi_{-101} + \psi_{-10-1} - \psi_{-110} + \psi_{-1-10}$
$E_{101}(u) = 4\pi^2 \{(u+1)^2 + 1\}$		$\psi = \psi_{101} + \psi_{10-1} - \psi_{110} - \psi_{1-10}$
	Γ_3	
$E_{011}(u) = 4\pi^2 (u^2 + 2)$		$\psi = \psi_{011} + \psi_{0-1-1} - \psi_{01-1} - \psi_{0-11}$
$E_{-211}(u) = 4\pi^2 \{(u-2)^2 + 2\}$		$\psi = \psi_{-211} + \psi_{-2-1-1} - \psi_{-21-1} - \psi_{-2-11}$
	Γ_4	
		has no representations for energies as low as those considered here.
	Γ_5	
$E_{-101}(u) = 4\pi^2 \{(u-1)^2 + 1\}$		$\psi = \psi_{-101} + i\psi_{-110} - \psi_{-10-1} - i\psi_{-1-10}$
		and
$E_{101}(u) = 4\pi^2 \{(u+1)^2 + 1\}$		$\psi = \psi_{-101} - i\psi_{-110} - \psi_{-10-1} + i\psi_{-1-10}$
		and
$E_{011}(u) = 4\pi^2 (u^2 + 2)$		$\psi = \psi_{101} + i\psi_{110} - \psi_{10-1} - i\psi_{1-10}$
		and
$E_{211}(u) = 4\pi^2 \{(u-2)^2 + 2\}$		$\psi = \psi_{101} - i\psi_{110} - \psi_{10-1} + i\psi_{1-10}$
		and
		$\psi = \psi_{011} + i\psi_{01-1} - \psi_{0-1-1} - i\psi_{0-11}$
		and
		$\psi = \psi_{011} - i\psi_{01-1} - \psi_{0-1-1} + i\psi_{0-11}$
		and
		$\psi = \psi_{211} + i\psi_{21-1} - \psi_{2-1-1} - i\psi_{2-11}$
		and
		$\psi = \psi_{211} - i\psi_{21-1} - \psi_{2-1-1} + i\psi_{2-11}$

⁹ Na: Reference 1 and 2. Li: F. Seitz, Phys. Rev. **47**, 400 (1935); J. Millman **47**, 286 (1935).

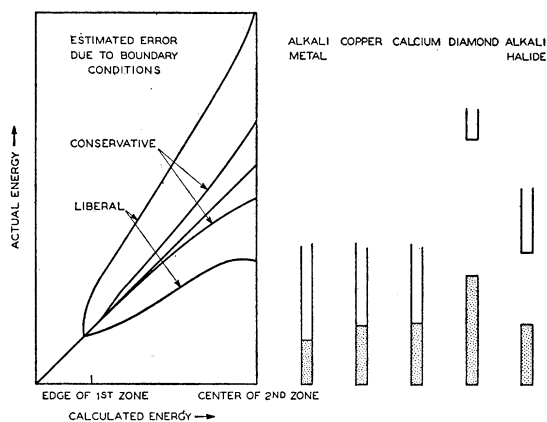


FIG. 3. Estimated error of the cellular method. For an energy calculated by the cellular method, the actual energy probably lies between the limits set by the liberal curves and outside those of the conservative curves. Computed energies for some solids reduced to the same scale are shown. Shaded regions represent occupied levels. Approximate band separations are shown for insulators.

errors due to the defects of the cellular method. For copper⁶ and calcium¹⁰ somewhat larger values are expected. For diamond¹¹ and the alkali halides¹² it is debatable whether the comparison should be made on a basis of lattice constant or spacing between neighboring atoms. From considerations of the number of expansion functions used per unit volume it appears more reasonable to use the lattice constant and the energy values are compared accordingly. We see that the band separations for both diamond and the alkali-halides are so large that we can feel certain of their independence from the particular approximations made. We see, however, that calculations of excited states, such as are needed in the theories of photoconductivity,

TABLE IV. *Symmetry types for the cellular solutions.*

Wave functions	Equation
$s, (x/r)p$	Γ_1 $\tan^2 \pi u/2 + \sigma/\pi = 0$
$(yz/r^2)d, (xyz/r^2)f$	Γ_3 $\tan^2 \pi u/2 + \delta/\varphi = 0$
$(xy/r^2)d, (xz/r^2)d, (y/r)p, (z/r)p$	Γ_5 $\tan^2 \pi u/2 + \delta/\pi = 0$

¹⁰ M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937).

¹¹ G. E. Kimball, J. Chem. Phys. **3**, 560 (1935); F. Hund, Physik. Zeits. **36**, 888 (1935).

¹² LiF: D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936); NaCl: W. Shockley, Phys. Rev. **50**, 754 (1936).

optical absorption, and fluorescence, cannot well be accurate.

It is interesting to compare the energy curves computed by Slater for Na with those of the empty lattice test. It is found that the two nearly coincide. From this we can deduce that exact solutions for Na will be very much like plane waves and that the energy discontinuities will be much smaller than those calculated. Slater has proposed a physical explanation for this phenomenon.¹³ He points out that the wave function in a lattice may be regarded as a solution of a scattering problem, each ion in the lattice acting as a scatterer. The less the scattering power of the ion, the nearer the wave function will be to a plane wave. Now the Na⁺ ion has the same electron configuration as neon, and it is well known that the rare gas atoms have abnormally small scattering cross sections for low velocity electrons—Ramsauer effect. Thus Slater concludes that the remarkably close approximation to plane waves of the Na wave functions can be regarded as the consequence of a Ramsauer effect in the crystal field.

In some cases, other information may indicate that the results of the cellular method are more accurate than indicated by Fig. 3. In Cu, for example, five *d* bands whose width is appreciably less than the entire occupied width are calculated. Since this is to be expected on the basis of the atomic energy levels, we can have more confidence in the structure of the *d* bands than if they came as unheralded results of the cellular method.

The energy scale of Fig. 3 should, of course, be compared in general with band widths rather than spacings between bands. Thus the energy scale of the x-ray levels would be enormous in the figure, however, the breadth of the levels would be extremely small. For this case then, where the Bloch method can be used with very satisfactory accuracy, we should expect the cellular method to give good results.

VI. CONCERNING IMPROVEMENTS IN THE CELLULAR METHOD

The cellular method of joining was originally proposed as a simplification of the problem of

¹³ Comments by J. C. Slater at the Symposium on the Structure of Metallic Phases at Cornell University, July 1, 2, 3, 1937.

constructing continuous lattice functions. Rather than requiring the function and its derivatives to be continuous over the entire intercellular boundaries, continuity of value and normal derivative at the midpoint only were demanded. In the body-centered lattice, in fact, only the eight octahedral faces of the cell were considered, no conditions being placed upon the six cubic faces. It is thus natural to seek improvements by imposing further continuity requirements.

Work on the body-centered lattice including the six cubic faces in the joining scheme has been undertaken by Manning and Chodorow.¹⁴ The six new conditions require the introduction of six additional surface harmonics. Elementary considerations indicate strongly that these should be the two d functions, $(x^2 - y^2)/r^2$, $(y^2 - z^2)/r^2$, the three f functions $(x^3 - \frac{3}{5}xr^2)/r^3$, $(y^3 - \frac{3}{5}yr^2)/r^2$, $(z^3 - \frac{3}{5}zr^2)/r^3$ and the one cubically symmetrical g function. No detailed tests with these new functions have been carried out, however, the following considerations show that no great improvement will result from their use. For $\mathbf{k} = 0$, we see that a triple solution is still obtained from old d functions which vanish on the cubic faces. The new d functions vanish on the octahedral faces and satisfy the boundary condition $\delta = 0$ on the cubic faces. The function $2x^2 - y^2 - z^2$ gives the point marked "14 point fitting" on the Fig. 2a. The other $y^2 - z^2$ gives a zero width band of type Γ_2 , a missing type for the previous work. If calculations for other values of \mathbf{k} were carried out these points would become energy curves; and the old curves, but not the end points for $\mathbf{k} = 0$, would be changed. It is readily seen that the resultant curves could not approximate the exact solutions with much improved accuracy.

For the face-centered lattice it is more natural to seek improvement by requiring continuity conditions in tangential derivatives at the midpoints of the faces. This gives four conditions for each pair of midpoints:

Value
$$Tu_\theta - u_u = 0. \tag{11}$$

Normal derivative
$$(\partial/\partial r)u_\theta + T(\partial/\partial r)u_u = 0. \tag{12}$$

¹⁴M. F. Manning and M. Chodorow, Phys. Rev. 50, 399A (1936).

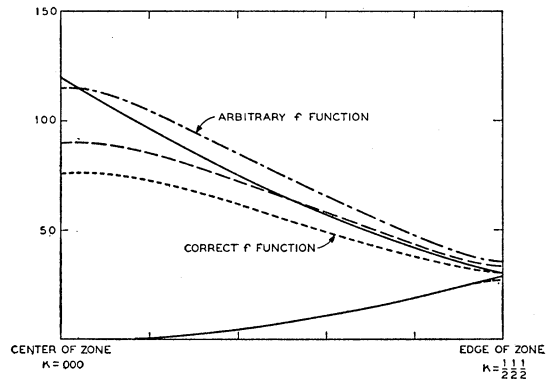


FIG. 4. Result of requiring continuity of tangential derivatives at midpoints of intercellular faces for the 111 direction of the face-centered lattice. Solid line, exact solution; dashed line, old cellular solution; dotted line, new cellular solution using zonal f function; dashed and dotted line, new cellular solution using arbitrary f function.

Tangential derivative

$$(\partial/\partial\theta)u_\theta + T(\partial/\partial\theta)u_u = 0. \tag{13}$$

Tangential derivative

$$(\partial/\partial\varphi)u_\theta + T(\partial/\partial\varphi)u_u = 0. \tag{14}$$

θ and φ are polar coordinates whose axes may be chosen according to convenience and $T = \tan 2\pi\mathbf{k} \cdot \mathbf{r}$ where \mathbf{r} is the radius vector to the midpoint of the face. The functions and derivatives are evaluated at the midpoint.

For the 111 direction, it is convenient to let $\theta = 0$ for 111 and $\varphi = 0$ for 100. Due to the symmetry of 111, it is sufficient to satisfy the boundary conditions for any given symmetry type only upon 011 and 01 $\bar{1}$ that is $\cos \theta = (\frac{2}{3})^{\frac{1}{2}}$, $\varphi = \pi$ and $\theta = \pi/2$, $\varphi = \pi/2$. For Γ_1 which is the simplest symmetry type u_u , $\partial u_\theta/\partial\theta$, $\partial u_\theta/\partial\varphi$ and T vanish on 01 $\bar{1}$, so that all but the normal derivative conditions are fulfilled trivially. On 011 the derivatives in respect to φ vanish but those in respect to θ do not. Thus only one new condition arises. In order to satisfy it we must introduce one additional function of type Γ_1 . There are two such f -functions: $(\cos^3 \theta - 3 \cos \theta/5)f$ and $\sin^3 \theta \cos 3\varphi f$. It is most natural to choose the first function since it is the one which occurs in the expansion of a plane wave in the 111 direction. It is readily verified that both functions have the same value for $(\partial\psi/\partial r)/\psi = \varphi$ at the joining point and values of $-21 \times 2^{\frac{1}{2}}$ and $+3 \times 2^{\frac{1}{2}}$ respectively for $\varphi' \equiv (\partial\psi/\partial\theta)/\psi$.

The determinantal equation for the continuity condition may be set up in the usual way and reduced to¹⁵

$$\tan^2 \pi u = -\frac{2\delta(1+1/2^{1/2}\varphi') + (\varphi - \pi)2 \times 2^{1/2}/\varphi'}{(\pi + \varphi/2^{1/2}\varphi')(1 + \delta/\sigma)}. \quad (15)$$

This is to be compared with the equation

$$\tan^2 \pi u = -2\delta/\pi(\delta/\sigma + 1), \quad (16)$$

which is obtained in the absence of tangential boundary conditions. Due to smallness $1/\varphi'$, π/φ' and φ/φ' for energies in the first zone, the new expression is equivalent to the old. In the second zone, however, the results, shown in Fig. 4, using the first f function ($\varphi' = -21 \times 2^{1/2}$) are actually worse than the old. From a suitable linear combination of the two f functions any desired value of φ' can be obtained. The arbitrarily chosen value 10.8 gives the curve which fits the correct parabola fairly well.

VII. CONCLUSIONS

The results of the cellular method of finding wave functions are probably quite good for the occupied states of the metals so far calculated.

¹⁵ The reader is referred to references 2, 5 and 6 for the general method of setting up the determinantal equations of the cellular method.

For excited states, however, very large errors are to be expected. This cannot be overcome by such simple expedients as adding a few more joining conditions to those already in effect. It appears that the number of new conditions necessary to take care of higher energies would make the labor of calculation prohibitively difficult. However, a new method of attack has been proposed by Slater and it is to be hoped that it will circumvent these difficulties.

Finally it should be remarked that this work has been concerned with only one aspect of the electronic theory of solids. Although accurate solutions of the wave equation in the crystal would be very valuable they suppose that each electron sees a static potential field in which the influence of the other electrons is represented by an average. Actually relative positions of the electrons, correlation effects, must be considered in order to explain many properties, for example the binding energy of the alkali metals¹⁶ and the phenomenon of excitation in insulators.¹⁷

The writer would like to express his gratitude to Professor Slater, under whose direction work on this problem was commenced, and whose continued interest has been instrumental in its completion.

¹⁶ E. Wigner, Phys. Rev. **46**, 1002 (1934).

¹⁷ J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936).

Theory of the Use of More Than Two Successive X-Ray Crystal Reflections to Obtain Increased Resolving Power

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If an x-ray beam is selectively reflected from more than two crystal surfaces in succession it is shown in this paper by a simple method of graphical analysis that it should be possible to obtain resolving power considerably superior to the best obtainable with present two crystal x-ray spectrometers. This extension and generalization of the two crystal spectrometer principle in one of its forms (the three crystal spectrometer) should permit the study of the asymmetric diffraction patterns predicted by the theory of Prins but heretofore considered to be completely beyond experimental investigation. In another form (the four crystal spectrometer) a distinct improvement in spectral resolving power is anticipated. The new method of graphical analysis invented for the purpose of discussing these more complicated cases of polycrystalline x-ray reflection is conspicuously useful and clear as a help to understanding the two crystal spectrometer also. An experimental test of these new methods is now in progress.