

## Energy Bands of Aluminum

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The Green's function method for investigating the band structure of crystals is applied here to aluminum. The potential used in the calculations is close to that employed by Heine, the difference consisting of a correction and a small modification required for the simple application of the Green's function method. Extensive calculations were made in order to study the convergence of the energies and wave functions and the perturbation arising from the use of the "muffin-tin" potential instead of the originally determined  $V(\mathbf{r})$ . The convergence of the energies is shown to be very rapid; the convergence for the eigenfunctions is somewhat slower but is still satisfactory. The perturbations of the eigenvalues are shown to be smaller than the errors expected as a result of the inaccuracies in the present potential, which is known comparatively

accurately. The relative separations of the calculated levels are in good agreement with those for Heine's result except for his upper  $K_1$  level which is about 0.25 ry too high. Our energies lie about 0.1 ry below Heine's as a result of the correction to the potential. It is shown that the calculated eigenvalues can be fitted remarkably well for filled and low-lying excited states by a nearly free electron (pseudopotential) interpolation scheme. It is also shown that the Bloch functions can be determined in a simple fashion from the nearly free electron scheme. By virtue of the similarity of the present bands with those Harrison obtained by the pseudopotential interpolation procedure, we conclude that the shape of the Fermi surface associated with the present results is consistent with available experimental data.

### I. INTRODUCTION

IN the first of this group of papers,<sup>1</sup> the application of the Green's function method for studying the band structure of solids was discussed in some detail. As a mathematical test of the method, the three-dimensional Mathieu problem—the only nontrivial three-dimensional problem for which exact solutions are known—was studied there. An earlier test had been carried out for a case in which the tight-binding approximation was applicable.<sup>2</sup> Here we are concerned with the more realistic problem of the band structure of aluminum. Ham<sup>3</sup> has dealt with the corresponding problem for the alkali metals. While the principal goal of these studies is the elucidation of the electronic structure of these metals, which is essential for the understanding of their physical properties, we have also endeavored to study the various aspects of the application of the Green's function method discussed in HS<sup>1</sup> to several different types of metals. With these two purposes in mind, we have made rather extensive studies. These include, in addition to the energies of the aluminum energy bands at a large number of points in the Brillouin zone, the calculation of the wave functions, and the perturbations arising from the use of the "muffin-tin" potential [HS Sec. V] instead of the original potential.

Aluminum was chosen to be investigated by this method for several reasons. Of primary importance is the interest in the physical properties of metal. Closely associated with this is the existence of a substantial body of experimental data bearing on the band structure in general and the Fermi surface in particular that come primarily from the de Haas-van Alphen, cyclotron resonance, anomalous skin effect, specific heat, and ultrasonic attenuation measurements. It is of consider-

able importance to see if a careful band calculation can yield results consistent with the above-mentioned data. Harrison,<sup>4</sup> using essentially an interpolation scheme and Heine's<sup>5</sup> symmetry point energies, was successful in obtaining a Fermi surface that appears to be in good agreement with experiment. It is our purpose to determine the  $E(\mathbf{k})$ —and hence the Fermi surface—directly from the Schrödinger equation with a realistic crystal potential.

In the past, theoretical investigations of polyvalent crystals have been, in general, considerably less successful than those for the alkalis largely due to the greater difficulty of determining the fields acting on the valence electrons in the polyvalent solids. Hence, interest attaches to an attempt to do a careful calculation of these materials. One such study of Al was undertaken by Heine<sup>5</sup> using the orthogonalized plane wave method. In this extensive work, Heine made a rather careful calculation of the crystalline potential which his results indicated was at least to some degree self-consistent. It was later shown by Behringer<sup>6</sup> that one of the contributions to his potential, albeit not one of the large ones, was incorrect. Also, some doubt was cast about one of his eigenvalues at the important symmetry point,  $K [(a/2\pi)\mathbf{k} = (\frac{3}{4}, \frac{3}{4}, 0)]$  near the Fermi surface.<sup>4</sup> It was thus felt that it would be very desirable to compare the results of a careful calculation employing the Green's function method with Heine's results.

Another point about Heine's work that is worth commenting on concerns the difficult and unsettled question of the correlation and exchange corrections which Heine treated on the basis of the first-order Bohm-Pines theory. It is very doubtful that such a treatment is quantitatively correct for real metals. In Sec. IV, we discuss this point briefly and also give arguments for why we believe that the many-body corrections should not be included in calculations like the present one.

<sup>1</sup> F. S. Ham and B. Segall, preceding paper [Phys. Rev. **124**, 1786 (1961)]. This paper will hereafter be referred to as HS, and, for example, Eq. (2.15) of that paper will be indicated by (HS2.15).

<sup>2</sup> B. Segall, J. Phys. Chem. Solids **8**, 371 (1959).

<sup>3</sup> F. S. Ham (to be published).

<sup>4</sup> W. A. Harrison, Phys. Rev. **118**, 1182 (1960).

<sup>5</sup> V. Heine, Proc. Roy. Soc. (London) **A240**, 361 (1957).

<sup>6</sup> R. E. Behringer, J. Phys. Chem. Solids **5**, 145 (1958).

A striking feature of the energy bands reported on here is their close resemblance to the bands of a free electron, the differences being essentially the small splittings of the degeneracies specific to free electron bands. This relates to the work of Harrison,<sup>4</sup> who on the basis of Heine's symmetry point energies inferred that a "nearly free electron" (a pseudopotential) interpolation scheme would be applicable to aluminum. With our much more extensive calculations we were able to thoroughly investigate this approach and have found it to be valid for the occupied and low-lying excited states.

Further, we have investigated the relationship between the detailed Bloch functions and the nearly free electron eigenfunctions, and have found that the Bloch functions can be determined fairly accurately and easily from the simple functions. This fact can be very useful in future calculations of the properties of this metal.

The results of the calculations described in this paper clearly demonstrate the validity of the claims made in HS regarding the usefulness of the Green's function method in obtaining detailed information about the electronic structure. The convergence of the eigenvalues has been shown to be very rapid, that for the eigenfunctions somewhat slower but still satisfactory. Finally the perturbations arising from the use of the muffin-tin potential have been shown to be smaller than the errors expected from our incomplete knowledge of the relatively well-known potential for Al.

A comparison is made with results of Heine,<sup>5</sup> who calculated the energies at the symmetry points. Aside from a shift of all his eigenvalues upward due to the previously cited error in his potential, the relative separations of the levels found here are generally in quite good accord with his. The one exception is his upper  $K_1$  root which is much too high.

In the next section we discuss the potential that was employed in these calculations. Section III contains the results of the calculations for the eigenvalues, eigenfunctions, and perturbations, along with the application of nearly free electron approximation. In Sec. IV we conclude with a discussion of the results and the method.

## II. POTENTIAL

Now that there exist powerful methods for solving the eigenvalue problem in a three-dimensional periodic potential, the critical and most difficult remaining problem is that of determining the appropriate crystalline potential. In this paper we assume the validity of the Hartree-Fock, or one electron approach, or at least that the many-body aspects can be handled approximately by a contribution (possibly  $\mathbf{k}$  dependent) to the potential [e.g., see contribution (vi) below]. We will thus not discuss in detail the basic but difficult problem concerning electron correlations.

The problem of obtaining a realistic potential for

Al is of interest, even though it is one of the simpler multivalent metals, because it involves some features that are not present in the case of the simplest metals, the alkalis, where the potentials are most well understood. The atomic configuration of an alkali atom consists of a single valence electron outside a tightly bound core which is essentially unaffected by the metallic binding. In studying these metals one generally introduces the Wigner-Seitz assumption which is that the potential acting on the electron is that due to the ion core within the cell. This simplification is further exploited in the quantum defect method<sup>7</sup> in which the explicit use of a potential is obviated by utilizing atomic spectra to determine the logarithmic derivatives of the radial wave functions.

In the case of a polyvalent material, however, since the fields that act on a valence electron depend in an important way on the distribution of the other valence electrons, and since the valence wave functions are significantly different in the solid than they are in the free atom, the previously mentioned simplicity does not exist. Here, for example, the quantum-defect method cannot be used, at least not in a straightforward manner. It is then necessary to construct an explicit potential.

The fact that the core in Al occupies only about 10% of the cell volume simplifies the determination of the potential. A further important simplification results from the assumption that the energy bands and the wave functions outside the core exhibit free electron behavior. It is important that these assumptions be justified in order that the claim for the potential's accuracy be made convincing. Our justification is that the results of our band-structure studies will be shown to be quite consistent with the assumptions.

The potential that was used in the calculations that we are reporting on is very close to that determined by Heine<sup>5</sup> in his extensive study of this problem. We refer the reader to his paper for the details. Except for the differences between his potential and the one used in this work, we will confine ourselves to a brief enumeration and comments on the various contributions that make up the potential. They are:

- (i) The contribution of the ion core as determined from the Hartree-Fock equations.
- (ii) A correction for correlation among the core electrons. This contribution is probably not very precise; but since it is small compared to the total, it cannot lead to any significant error.
- (iii) The contribution due to the exchange interaction of an  $s$  and a  $p$  wave function with the ion cores. The difference between the terms for the  $s$  and  $p$  functions is small over the most important part of the region of integration.
- (iv) The potential due the conduction electrons in one "atomic" sphere (i.e., a sphere whose volume equals

<sup>7</sup> T. S. Huhn and J. H. Van Vleck, *Phys. Rev.* **79**, 382 (1950); H. Brooks and F. S. Ham, *Phys. Rev.* **112**, 344 (1958).

that of the cell). The charge density of electrons for a given  $\mathbf{k}$  is assumed given by a single orthogonalized plane wave. The resultant contribution is averaged over a Fermi distribution.

(v) A correction to (iv) resulting from the fact that the charge distribution of electrons in the metal is not the sum of charge densities centered at the lattice sites which drop to zero outside the atomic spheres. As mentioned in the Introduction, this contribution was computed incorrectly by Heine. For this term we use the values given by Behringer.<sup>6</sup>

(vi) The final contribution is that due to the correlation and exchange among the conduction electrons. This term was computed by the first-order Bohm-Pines<sup>8</sup> theory which attempts to take into account the fact that the correlation and exchange "holes" move with the electrons. This contrasts with the Wigner-Seitz approach in which the hole is fixed at the nucleus. Heine writes this contribution as

$$V_{BP}(\mathbf{k}) + V_{ee}(\mathbf{r}),$$

where  $V_{ee}$ , the so-called exchange correction, is rather small and the more important term,  $V_{BP}(\mathbf{k})$ , is independent of  $\mathbf{r}$ . The term  $V_{BP}$  can then be treated as a correction to the energy. In the work that follows, the crystal potential that we will employ will not include this term, and the energies given will be for that crystal potential except where the addition of the  $V_{BP}$  correction is specifically indicated. This procedure is advantageous as our results (those without the  $V_{BP}$  term) are then not dependent on the doubtful validity of the first-order Bohm-Pines theory.

TABLE I. The "charge" for a single "atomic" sphere,  $2Z(r) = -rU(r)$ , and for the "muffin-tin" potential,  $2Z_{mt}(r) = -rV_{mt}(r)$ .

$r$ (a.u.)	$2Z(r)$ ( $l=0$ )	$2Z(r)$ ( $l=1$ )	$2Z_{mt}(r)$ ( $l=0$ )	$2Z_{mt}(r)$ ( $l=1$ )
0	26.00	26.00	26.00	26.00
0.005	25.65	25.64	a	b
0.01	25.29	25.28	a	b
0.02	24.60	24.56	a	b
0.04	23.28	23.18	a	b
0.06	22.09	21.90	a	b
0.10	20.10	19.70	a	b
0.15	18.08	17.48	a	b
0.20	15.41	15.66	a	b
0.30	12.80	12.77	a	b
0.40	10.61	10.59	a	b
0.60	7.865	7.917	a	b
0.80	5.451	5.651	a	b
1.0	3.712	3.543	a	b
1.2	3.232	3.161	a	b
1.4	2.722	2.683	a	b
1.6	2.263	2.239	a	b
2.0	1.513	1.504	1.553	1.544
2.5	0.881	0.877	1.091	1.087
3.0	0.385	0.384	1.001	1.000

<sup>a</sup> Same as  $2Z(r)$  ( $l=0$ ).

<sup>b</sup> Same as  $2Z(r)$  ( $l=1$ ).

<sup>8</sup> D. Pines, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 368.

TABLE II. The coefficients of the fourth- and sixth-order harmonics,  $V_4(|\mathbf{r}|)$  and  $V_6(|\mathbf{r}|)$ , of the crystal potential,  $V(\mathbf{r})$ .

$r$ (a.u.)	$V_4(r)$ (ry)	$V_6(r)$ (ry)
1.6	0	0
1.8	0.0005	0.0012
2.0	0.0031	0.0076
2.2	0.0100	0.0219
2.4	0.0218	0.0404
2.6	0.0314	0.0508
2.8	0.0396	0.0514

The sum of contributions (i) to (vi) yields the potential in the form

$$V(\mathbf{r}) = \sum_s U(|\mathbf{r} - \mathbf{r}_s|). \quad (1)$$

In the second and third columns of Table I we have tabulated  $2Z(r) = -rU(r)$  for the  $l=0$  and 1 potentials at a fraction of the points that were employed in the computations. The potentials for  $l \geq 2$ , aside from the centrifugal term,  $r^{-2}l(l+1)$ , are taken equal to  $l=0$  potential.

From Heine's estimates, the approximate potential is expected to lead to errors amounting to a few hundredths of a rydberg in the relative positions of the levels.

The procedure for appropriately determining the muffin-tin potential  $V_{mt}(\mathbf{r})$  and the perturbing potential,  $\delta V(\mathbf{r}) = V(\mathbf{r}) - V_{mt}(\mathbf{r})$ , for a potential of the form Eq. (1), is given in Sec. V and Appendix II of HS. The quantities  $2Z_{mt}(r) = -rV_{mt}(r)$  for  $l=0$  and 1 are given for  $r < r_i$  in the fourth and fifth columns of Table I. In order to investigate the perturbations we have computed  $V_4(r)$  and  $V_6(r)$  which are defined in HS 5.1, and have tabulated them in Table II. In Table III we have listed the first few Fourier coefficients for  $\delta V(\mathbf{r})$  (HS A2.7). Finally, we have determined the constant potential,  $V_e$ , to be  $-0.273$  ry.

### III. RESULTS OF THE CALCULATIONS

#### 1. The Energies

Aluminum crystals have the face-centered cubic structure and the related Brillouin zone is the truncated octahedron illustrated in Fig. 1. In this work we will use the notation introduced by Bouckaert *et al.*<sup>9</sup> for

TABLE III. The Fourier coefficients of the difference between the crystal potential,  $V(\mathbf{r})$ , and the "muffin-tin" potential,  $V_{mt}(\mathbf{r})$ .

$(a/2\pi)\mathbf{K}_n$	$V(\mathbf{K}_n)$ (ry)
(1,1,1)	-0.00755
(2,0,0)	-0.0117
(2,2,0)	+0.00572
(3,1,1)	-0.00440
(2,2,2)	-0.00486

<sup>9</sup> L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

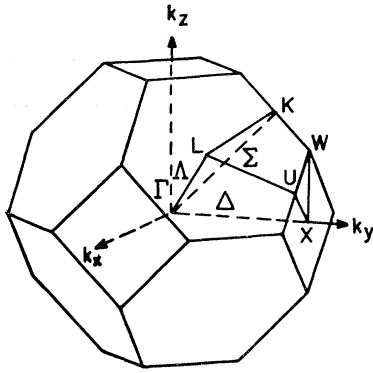


FIG. 1. The Brillouin zone for the fcc structure with points and lines of high symmetry.

the symmetry points and lines and the irreducible representations associated with them.

The procedures used in the calculations of the energies and wave functions are those discussed in Secs. III and IV of HS. For computations with the large matrices an IBM 704 digital computer was used. In an endeavor to study the convergence we have included harmonics with  $l \leq 6$  in the trial functions. A typical example of the rapid convergence is illustrated in Table IV for the  $\Delta_1$  root for  $\mathbf{k} = (2\pi/a)(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$ . Comparable behavior was observed for the other eigenvalues studied here and in Ham's<sup>3</sup> work on the alkalis.

To compare our results with those of Heine<sup>5</sup> we first determined the energies for the symmetry points using a muffin-tin potential based on exactly the same  $V(\mathbf{r})$  that he employed. The comparison is provided by Table V where Heine's<sup>5</sup> results (with the Bohm-Pines correction subtracted out) are given in the second column and the present results in the third column. In general there is quite good agreement between the two sets of energies. However, our third zone  $K_1$  value is more than three volts lower than his. This large discrepancy, which Harrison<sup>4</sup> noted from his interpolation calculations, persists in the comparison with the computations with the "corrected" potential. Our  $K_1$  value is further

TABLE IV. Convergence of the  $\mathbf{k} = (2\pi/a)(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$  eigenvalue.

$l_{\max}$	$E(\text{ry})$
0	-0.105
1	-0.1723
2	-0.1799
3	-0.1801
4	-0.1801
5	-0.1801
6	-0.1802

confirmed by the continuity of neighboring energies on the  $\Sigma_1$  axis.

The principal calculations were performed using the muffin-tin potential based on the  $V(\mathbf{r})$  determined from Table I, i.e., including the corrected values of the contribution (v) of Sec. II. The eigenvalues were computed for many points on the  $\Delta$ ,  $\Lambda$ , and  $\Sigma$  axis, i.e., the  $[100]$ ,  $[111]$ , and  $[110]$  axes, respectively, in the interior of the Brillouin zone and on the  $Z$  and  $S$  axes on the square face. The energies at the symmetry points for the "corrected" potential, which are listed in the fourth column of Table V, are seen to lie generally about 0.1 ry lower than Heine's. More interesting than the absolute values are the relative positions of the levels. The sixth and seventh columns give the separation of the levels from  $\Gamma_1$ , the state at the center of the first zone, for Heine's and the present calculation, respectively. For these values we find substantial accord between the two sets of results except, again, for the  $K_1$  value in the third zone for which Heine's value is much too high.

A point of interest in the study of metals like aluminum is whether or not the energy bands have a free-electron character. Figure 2, in which the calculated energies for points on the  $\Delta$ ,  $\Lambda$ , and  $\Sigma$  are simultaneously plotted against  $|\mathbf{k}|$ , throws light on this point. It is immediately evident that  $E(\mathbf{k})$  is quite spherically symmetric except for small regions near the zone surface where the effects of the gaps are manifested. Neglecting

TABLE V. The energies<sup>a</sup> for the states of high symmetry in aluminum.

State	Heine's Energies <sup>b</sup>	$E_A$ , present results for <sup>c</sup> $V_{\text{Heine}}$	$E_B$ , present results for <sup>d</sup> $V_{\text{corr}}$	$E_B + V_{\text{BP}}^e$	$E - E(\Gamma_1)$ (Heine)	$E_B - E_B(\Gamma_1)$
$\Gamma_1$	-0.377	-0.390	-0.463	-0.966	0	0
$X_4'$	0.215	0.239	0.159	-0.166	0.592	0.622
$X_1$	0.340	0.313	0.235	-0.087	0.717	0.698
$W_1$	0.572	0.578	0.460	0.158	0.949	0.923
$W_2'$	0.449	0.422	0.356	0.054	0.826	0.819
$W_3$	0.397	0.396	0.313	0.011	0.774	0.776
$L_2'$	...	0.092	0.020	-0.325	...	0.483
$L_1$	...	0.140	0.049	-0.296	...	0.512
$K_3$	0.322	0.320	0.236	-0.076	0.699	0.699
$K_1$	0.365	0.367	0.260	-0.052	0.742	0.723
$K_1$	0.698	0.452	0.339	0.027	1.075	0.802

<sup>a</sup> The unit of energy is the rydberg (=13.60 ev).

<sup>b</sup> V. Heine, reference 5. The values tabulated here do not include the Bohm-Pines correction.

<sup>c</sup>  $V_{\text{Heine}}$  is the "muffin-tin" potential based on Heine's potential.

<sup>d</sup>  $V_{\text{corr}}$  is the potential described in Sec. II.

<sup>e</sup>  $V_{\text{BP}}$  is the Bohm-Pines correction.



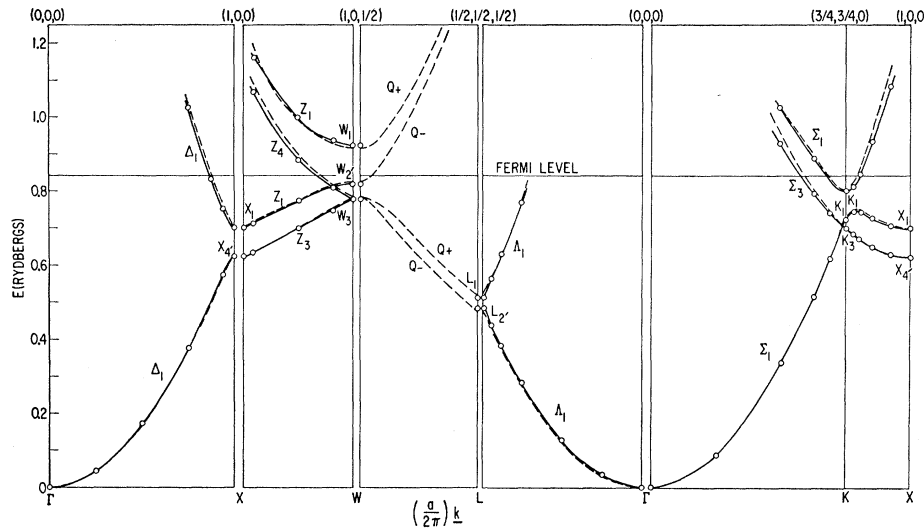


FIG. 4. The comparison of the "nearly free electron" (or "pseudopotential") interpolation scheme results with the calculated values. The solid curve passes through the circles which represent the calculated energies. The dashed curves represent the "nearly free electron" fit obtained with the following parameters:  $m^*/m_0=1.03$ ;  $V(1,1,1)=0.023$  ry, and  $V(2,0,0)=0.043$  ry.

smaller than 0.01 ry except for energies well above the Fermi level where they are somewhat larger. This demonstrates the validity of this approach for aluminum.

As discussed in Sec. II, the major part of the exchange and correlation contribution, (vi), to the potential determined by the Bohm-Pines theory is a spatially independent term  $V_{BP}(\mathbf{k})$ . This term which was not incorporated in the potential  $V(\mathbf{r})$ , Eq. (1), could be added directly to the eigenvalue. The energies for the symmetry points with the addition of  $V_{BP}(\mathbf{k})$ , which was evaluated using a "cutoff" parameter<sup>12,13</sup> of  $\beta=0.40r_s^{-1}=1.437$  (where  $r_s$  is in atomic units), are given in the fifth column of Table V. We have chosen to keep this contribution separate from the remainder of our results because we feel that it is probably the least soundly based aspect of this work. An indication of this is the fact that the second-order terms<sup>13</sup> which we have evaluated for aluminum are not sufficiently smaller than the first-order terms for all of the occupied states to warrant confidence that the corrections are convergent. In general it is probably correct to state that

at present there is no very satisfactory procedure for including the effects of correlation in calculations of a real solid.

## 2. Wave Functions

As discussed in Sec. IV of HS, the wave function for  $r < r_i$  is expanded in a series of lattice harmonics,  $\mathcal{Y}_{lj}(\mathbf{r})$ , and solutions of the radial Schrödinger equation,  $R_l(r)$ , according to (HS 2.8). The coefficients for  $l=0, 1$  and 2 were determined for  $\mathbf{k}$  along the  $[100]$  and  $[111]$  axes from the center of the zone to points near the Fermi surface. Since the wave function is not a stationary quantity, the convergence for the  $C_{lj}$  is not expected to be as rapid as for the energy. Nevertheless, it is rapid enough so that these coefficients can be conveniently determined to within a few percent for the states considered.

The values of the  $C_{lj}$ , of course, depend on the normalization of the  $R_l(r)$ . For this reason we have listed in Tables VI and VII the values of  $R_l(r)$  at the sphere radius along with the values of  $C_{lj}$ . The tabulated coefficients for the  $[100]$  axis are more precise than those for the  $[111]$  axis because of the inclusion of contributions from higher order harmonics in the former.

TABLE VI. The expansion coefficients of the wave functions in the region  $r < r_i$  for states with  $\mathbf{k}$  in the  $[100]$  direction. The  $R_l(r_i)$  are the radial functions evaluated at the inscribed sphere radius.

$(a/2\pi)\mathbf{k}$	$C_0$	$C_1$	$C_2$	$R_0(r_i)$	$R_1(r_i)$	$R_2(r_i)$
$(\frac{1}{2}, 0, 0)$	1.0	-1.71	0.14	1.679	-0.322	0.576
$(\frac{3}{2}, 0, 0)$	1.0	-3.53	0.58	1.520	-0.302	0.530
$(\frac{5}{2}, 0, 0)$	1.0	-5.84	1.49	1.269	-0.271	0.460
$(1, 0, 0) X_4'$	0	1.0	0	...	-0.233	...
$(1, 0, 0) X_1$	1.0	0	3.64	0.909	...	0.364
$(\frac{3}{2}, 0, 0)$ 2nd zone	1.0	7.15	4.99	0.768	-0.202	0.328
$(\frac{5}{2}, 0, 0)$ 2nd zone	1.0	9.80	7.58	0.587	-0.175	0.283

<sup>12</sup> The interelectronic spacing,  $r_s$ , is defined by  $(\frac{4}{3})\pi r_s^3 = \rho_0^{-1}$ , where  $\rho_0$  is the average valence electron density.

<sup>13</sup> J. G. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958).

TABLE VII. The expansion coefficients of the wave functions in the region  $r < r_i$  for states with  $\mathbf{k}$  in the  $[111]$  direction. The  $R_l(r_i)$  are the radial functions evaluated at the inscribed sphere radius.

$(a/2\pi)\mathbf{k}$	$C_0$	$C_1$	$C_2$	$R_0(r_i)$	$R_1(r_i)$	$R_2(r_i)$
$(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$	1.0	-1.47	0.10	1.692	-0.323	0.580
$(\frac{2}{3}, \frac{2}{3}, \frac{2}{3})$	1.0	-3.00	0.43	1.572	-0.309	0.545
$(\frac{4}{3}, \frac{4}{3}, \frac{4}{3})$	1.0	-4.75	0.86	1.379	-0.285	0.490
$(\frac{5}{3}, \frac{5}{3}, \frac{5}{3})$	0	1.0	0	...	-0.254	...
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) L_2'$	1.0	0	2.33	1.113	...	0.417
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) L_1$	1.0	6.9 <sup>a</sup>	3.3 <sup>a</sup>	0.984	-0.232	0.383
$(\frac{7}{6}, \frac{7}{6}, \frac{7}{6})$ 2nd zone	1.0	8.23	4.65	0.836	-0.212	0.345

<sup>a</sup> These values are less accurate than the others because the energy of the state is close to a free-electron singularity in the Green's function.

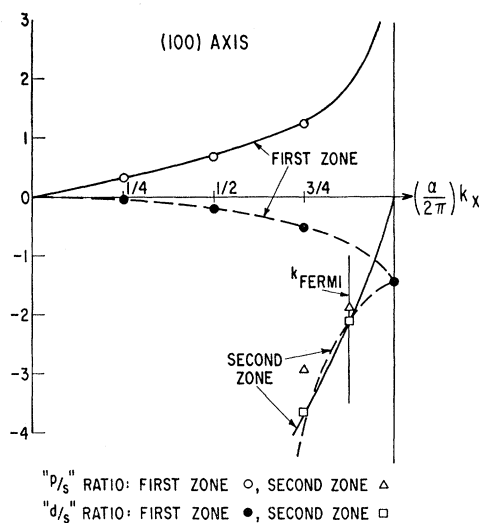


FIG. 5. The relative amplitudes of the  $l=0, 1$ , and  $2$  harmonics of the wave functions at the inscribed sphere radius for  $\mathbf{k}$  in the  $[100]$  direction. The ratios obtained from the detailed band calculations are indicated by the small geometric symbols (e.g.,  $\circ$  and  $\triangle$ ). The solid curves represent the  $p$  to  $s$  ratios for the "nearly free electron" scheme used to fit the energy bands, while the dashed curves give the  $d$  to  $s$  ratios.

In view of the success of the nearly free electron model in describing the energy bands, it is natural to inquire whether the wave functions also exhibit some free electron character. It is obvious that within the core region there will be little resemblance between the correct wave function and free or nearly free electron eigenfunctions because of the large fields and the related atom-like oscillations of the correct functions that exist there. However, outside the core, say in the region near the inscribed sphere, the fields are not rapidly varying.

With this in mind we have computed the ratios of the

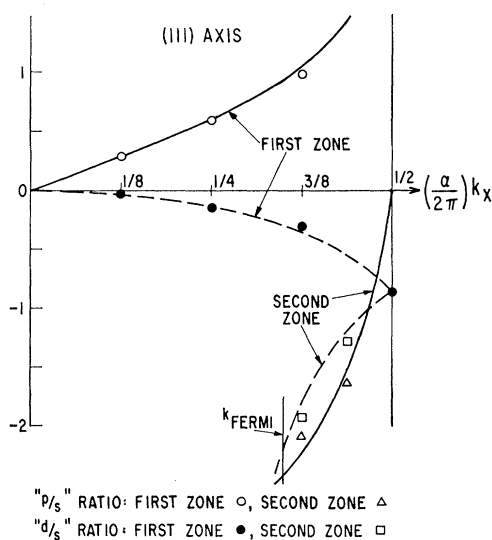


FIG. 6. The relative amplitudes of the  $l=0, 1$ , and  $2$  harmonics of the wave functions for  $\mathbf{k}$  in the  $[111]$  direction. The symbols and curves have the same significance as in Fig. 5.

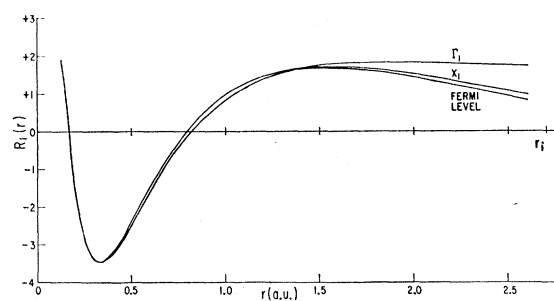


FIG. 7. The  $l=0$  radial functions,  $R_0(r)$ , for the energies of the  $\Gamma_1$ ,  $X_1$ , and Fermi levels.

magnitudes of the  $p$  and the  $d$  components to the  $s$  components of the wave function at the inscribed sphere, i.e.,  $C_l R_l(r_i)/C_0 R_0(r_i)$  for  $l=1$  and  $2$ . These were compared with the corresponding quantities for the nearly-free electron case. For the latter, the ratios of the  $p$  and  $d$  to the  $s$  component are given simply by

$$(2l+1)^{1/2} \left\{ \frac{j_l(|\mathbf{k}|r) + (-)^l b(\mathbf{K}) j_l(|\mathbf{k}+\mathbf{K}|r)}{j_0(|\mathbf{k}|r) + b(\mathbf{K}) j_0(|\mathbf{k}+\mathbf{K}|r)} \right\} \bigg|_{r=r_i}, \quad (2)$$

where  $b(\mathbf{K})$  is the amplitude of the Bragg reflected wave and  $j_l(x)$  is the spherical Bessel function of order  $l$ . The ratios determined from the detailed calculations are given in Fig. 5 for the  $\Delta$ -axis and in Fig. 6 for the  $\Lambda$  axis, while the values obtained from (2) using the amplitudes  $b(\mathbf{K})$  required for the energy band interpolation are indicated by the curves. Here again, the agreement is very good.

From these results we can reasonably expect to determine the wave function for an arbitrary state (i.e., any  $\mathbf{k}$  in the zone) with fair accuracy from the nearly free electron model and the radial functions of the corresponding energy. This fact is important because it makes feasible the calculation of matrix elements between proper Bloch functions for arbitrary  $\mathbf{k}$  which are required in the study of the various physical properties of the metal.

In Figs. 7 and 8 we show the radial functions for  $l=0$  and  $l=1$  for a few of the important energies.

### 3. Wave Functions Outside the Sphere

In HS Sec. IV, the method for determining the wave function for  $r > r_i$  in the form of a Fourier series was

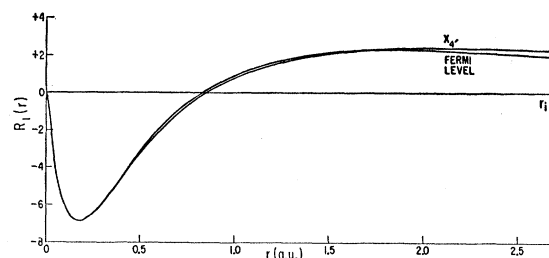


FIG. 8. The  $l=1$  radial functions,  $R_1(r)$ , for the energies of the  $X_4'$  and Fermi levels.

TABLE VIII. The expansion coefficients for the normalized  $\Gamma_1$  wave function for  $r > r_i$ .

$(a/2\pi)\mathbf{K}_n$	$F_n$
(0,0,0)	+0.0975
(1,1,1)	+0.0007
(2,0,0)	-0.0002
(2,2,0)	-0.0009

presented. In this work the wave function for the center of the zone (i.e.,  $\mathbf{k}=0$ ,  $\Gamma_1$ , state) which included the plane waves with  $(a/2\pi)\mathbf{K}_n = (0,0,0)$ ,  $(1,0,0)$ ,  $(2,0,0)$ , and  $(2,2,0)$  was obtained. The coefficients of the plane waves,  $F_n$ , are given in Table VIII. It is noteworthy that the  $\mathbf{K}_n=0$  term is over one hundred times larger than the others. This reflects the fact that the wave function, and  $|\psi(\mathbf{r})|^2$ , are quite flat in the corners of the polyhedron.

The wave functions exterior to the inscribed sphere for the other symmetry points were not determined in such detail. Inasmuch as we were primarily interested in estimating the perturbations, we were content in those cases to determine the dominant linear combination of plane waves by the simple means described below.

#### 4. Perturbation

It is convenient and informative to consider separately the perturbations, arising from  $\delta V = V(\mathbf{r}) - V_{mt}(\mathbf{r})$ , for the regions inside and outside the inscribed sphere. For  $r < r_i$  the perturbing potential is  $V_4(|\mathbf{r}|)L_4(\mathbf{r}) + V_6(|\mathbf{r}|)L_6(\mathbf{r}) + \dots$  (HS 5.1). The major contribution to the energy shifts comes in the first-order perturbation from the  $l=2$  component of the wave function and the fourth-order Kubic harmonics in  $V(\mathbf{r})$ . Using the previous results for the wave functions (normalized by the procedure given in HS Sec. IV) and  $V_4(\mathbf{r})$  obtained from Table II, we have found the perturbations for  $r < r_i$  to be

$$\begin{aligned} &-4.1 \times 10^{-4} \text{ ry} \quad \text{for } L_1, \\ &-5.5 \times 10^{-4} \text{ ry} \quad \text{for } X_1. \end{aligned}$$

These values are negligible, being about one hundredth of the expected errors in the energy due to our incomplete knowledge of the original  $V(\mathbf{r})$ .

The perturbation due to  $\delta V(\mathbf{r})$  for  $r > r_i$  would, of course, be expected to be larger. The first-order shift for the  $\Gamma_1$  state can be evaluated in a straightforward manner from the Fourier expansions of  $\delta V(\mathbf{r})$  and the wave function as determined above. These are given in Tables II and VIII, respectively. In this manner we find  $\Delta E_1(\Gamma_1) = -9.0 \times 10^{-4}$  ry. This small value is understandable in terms of the constancy of  $|\psi(\mathbf{r})|^2$  and the fact that  $V_c$  is so chosen that  $\int \delta V(\mathbf{r}) d\tau$  vanishes.

Since the first-order term is so small, it is of interest to estimate the second-order term. This estimate was obtained by the same means utilized in obtaining

TABLE IX. The first-order perturbations of the eigenvalues arising from the use of the "muffin-tin" potential instead of the original potential.

State	$\Delta E^{(1)}$ (ry)
$\Gamma_1$	-0.00090
$L_2'$	0.007
$L_1$	-0.007
$X_4'$	-0.006
$X_1$	0.008
$W_3$	-0.003
$W_2'$	0.025
$W_1$	0.018

(HS 6.7); that is, the energy denominator in the second-order perturbation term is replaced by an average "excitation energy",  $\langle E_n - E_0 \rangle$ , so that the sum over intermediate states can be carried out. Taking the  $\langle E_n - E_0 \rangle$  to be about the separation of the first-excited  $\Gamma_1$  from the ground state ( $\approx 4$  ry) we find a second-order correction of approximately  $-4 \times 10^{-4}$  ry. The fact that this value (which in itself is small) is almost as large as the first-order term is not an indication of poor convergence, as the lower term is abnormally small for the reason stated above.

While the method just employed can be used for all points in zone, the wave function for  $r > r_i$  and the perturbation can be obtained for the other symmetry points, and in fact for all points on the zone surface, by a vastly simpler method. For one of these states, the principal component of the wave function in the "corners" of the cell is not a single plane wave but a certain linear combination of plane waves. In this case the first-order perturbation does not vanish, so that the principal term is sufficient for determining the perturbation to a reasonable approximation. For example, the dominant part of the  $X_4'$  wave function for  $r > r_i$  is

$$\psi(\mathbf{r}) \approx C \{ \exp[i\mathbf{k} \cdot \mathbf{r}] - \exp[i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{r}] \} = 2iC \sin(\mathbf{k} \cdot \mathbf{r}),$$

where  $\mathbf{K} = (2\pi/a)(2,0,0)$ . The constant  $C$  can readily be determined by using the device involving (HS 4.16), which permits us to compute the fraction of the normalization integral outside the sphere.

The perturbations of the states at  $X$ ,  $L$ , and  $W$  were computed directly using the functions thus obtained and are listed in Table IX. It is seen that our previous contention concerning the smallness of the perturbation due to the use of the muffin-tin potential is borne out by the fact that the perturbations are of the order of a hundredth of a rydberg. The second-order perturbations have also been estimated and they are  $10^{-3}$  ry or less. These shifts are smaller than the expected errors in the levels due to uncertainties in the original potential.

#### IV. DISCUSSION

There were two principal motivations for this work. The first was the desire to determine accurately the energy bands of aluminum. The second was to study



and assess the various aspects of the application of the Green's function method to a realistic energy band calculation. In regard to the latter, we have made rather extensive calculations of the energies, wave functions, and perturbations due to the use of the muffin-tin potential instead of the originally determined  $V(\mathbf{r})$ .

The calculations have demonstrated the contention made in HS concerning the very rapid convergence of the energies. It has been shown that by including harmonics with  $l \leq 2$  in the trial function we obtain results that are generally accurate to a few thousandths of a rydberg for the occupied states. Such accuracy is sufficient for most band calculations because of the inherent inaccuracies in the one-electron approach itself and in the determination of the crystalline potential.

The convergence of the eigenfunctions, while somewhat slower than the eigenvalues, since the eigenfunctions are not stationary quantities, is still satisfactory for most anticipated uses. For example, the  $l=0, 1$ , and  $2$  components in the expansion of  $\psi(\mathbf{r})$  for  $r < r_i$  can be determined to within a few percent for states in which these components are not very small.

In these calculations, we have sought to determine the inaccuracies resulting from the use of the muffin-tin potential instead of the original potential given by Eq. (1). To this end we have evaluated the first-order and estimated the second-order perturbations for a number of symmetry points. It has been shown that the energy corrections from  $\delta V = V(\mathbf{r}) - V_{\text{mt}}(\mathbf{r})$  for  $r < r_i$  are negligible, being of the order of  $5 \times 10^{-4}$  ry. In view of this, it would seem that the correction from the region inside the inscribed sphere will be unimportant even for less spherically symmetric cases. The  $\delta V(\mathbf{r})$  for  $r > r_i$  obviously leads to larger perturbations. The energy corrections (Table IX) are of the order of a hundredth of a rydberg—less than this for states below the Fermi level,  $E_F$ , and somewhat more for states above  $E_F$ . In all cases the corrections are less than the errors in the energies expected from the uncertainties in the original  $V(\mathbf{r})$ .

It can be argued that aluminum is a favorable case and that in many other solids the deviation from a constant potential for  $r > r_i$  will be larger. While this is probably correct, it is also true that for those cases the potential in the corners of the cell is not known as accurately, at least presently, as for aluminum. Thus the errors due to the original limited knowledge of the potential will, in most cases, be larger than those due to the use of the simplified potential. Here we might also refer to the computations for the Mathieu potential in HS Sec. VI. While in that case the  $\delta V(\mathbf{r})$  is rather large, the corrections to the energy levels are reasonably small. On the basis of these experiences, it appears that the muffin-tin potential would be quite satisfactory for most solids. Even when this is not the case, simple perturbation calculations of the type described above could easily handle most of the needed corrections.

We have found that once the structure coefficients

have been evaluated and the logarithmic derivatives of the radial functions have been computed, it is an easy task to compute the eigenvalues even on a desk computer. The convenience with which the large number (over 60) of accurate eigenvalues were determined, even though a large number of harmonics ( $l \leq 6$ ) were included in the trial functions to test the convergence, attests to the usefulness of the method. From this experience, we can conclude that it is completely feasible to study the energy bands for arbitrary points throughout the zone. In particular, one could determine the Fermi surface directly. Also, if the crystalline potential can be approximated reasonably by a muffin-tin potential, as we have demonstrated for aluminum, this method provides a very convenient means for achieving self-consistency.

As far as the specific results for aluminum with Heine's original potential are concerned, we have found generally good agreement with his results for the symmetry points. The one exception is the third zone  $K_1$  value for which Heine's value is about three volts too high. The energy values for the "corrected" potential (i.e., with the corrected values for contribution (v) in Sec. II) are displaced downwards by roughly 0.1 ry. However, the relative separations of the levels we have found are in reasonably good agreement with Heine's. With the exception of his  $K_1$  value which is again about three volts (0.25 ry) too high, the relative separations of his levels differ from ours by less than 0.03 ry. In concluding this comparison it should be noted that these calculations by the Green's function method have exhibited a more satisfactory convergence than even the careful OPW calculations (like Heine's) in which the core functions are treated properly.

Many  $E(\mathbf{k})$  for the occupied and low-lying excited bands have been calculated for  $\mathbf{k}$  along the principal symmetry axes. It has been shown that aside from the energy gaps at the zone surfaces and the lifting of the purely free electron degeneracies, the aluminum energy bands are very free electron-like. A pseudopotential interpolation scheme (the nearly free electron approach) was tested and was shown to be in remarkably good agreement with the detailed calculation throughout the Brillouin zone. This substantiates in detail Harrison's<sup>4</sup> contention that this approach can be used for the energy bands of this metal.

It is important that such an approach be justified in some detail for each metal to which it is to be applied as the scheme is not universally applicable. In the alkalis, for example, Ham<sup>3</sup> has shown that the procedure, at least in the simple fashion used above, is not valid over a range of energies comparable to that considered here. It is possible that a modification of the above approach might make it more generally applicable; but this will probably involve more adjustable parameters and, as a result, be less attractive.

We have also found from this work that for aluminum the nearly free electron interpolation scheme can be

employed to determine the detailed wave function. In view of the success of the interpolation procedure for  $E(\mathbf{k})$  it is not surprising that a nearly free electron eigenfunction represents  $\psi(\mathbf{r})$  quite well in the corners of the polyhedral cell. Within the core region, of course, this simple function cannot be expected to be satisfactory at all. However, we have shown that the coefficients for the expansion of  $\psi(\mathbf{r})$  for  $r < r_i$  in terms of lattice harmonics—and, as a result,  $\psi(\mathbf{r})$  itself—can be determined reasonably accurately and simply from the nearly free electron procedure. This has the important consequence that matrix elements between proper Bloch states associated with various physical properties can be evaluated with enough precision to be useful for realistic studies of these properties. Because of the simplicity of this procedure it is even feasible, for example, to carry out averages of matrix elements over the Fermi surface.

In view of the fact that the potential [which is essentially Heine's plus the correction to (v)] appears to be accurate and the eigenvalues are given rather precisely, the results of these calculations should accurately portray the band structure of aluminum apart from the many-electron contributions. It appears, moreover, that these correlation effects do not substantially alter the shape of the Fermi surface for this metal. This follows from the similarity of the energy bands calculated here and the nearly free electron interpolation results of Harrison<sup>4</sup> which lead to a Fermi surface in accord with the experimentally determined one.

There remains the question of whether the effective masses derived from the calculated bands are, or should be, in agreement with the observed values. The masses obtained by Harrison were only about one-half the cyclotron resonance values reported by Langenberg and Moore.<sup>14</sup> The most disturbing disagreement is for the mass for the orbit about the second band surface for which the calculations gave a value of  $0.8m_0$ ,<sup>15</sup> while experiment indicated  $1.5m_0$ . Subsequently, Fawcett<sup>16</sup> reported finding a smaller mass in better agreement with the computed one. Most recently, however, Moore<sup>17</sup> has restudied aluminum using much purer samples and has apparently definitely reconfirmed the larger value.

This discrepancy is not unexpected and, in fact, it should occur since the observed masses involve contributions from the electron-electron and electron-phonon interactions. It is believed that the sum of both of these effects would be appreciable and of the correct sign,

<sup>14</sup> D. N. Langenberg and T. W. Moore, Phys. Rev. Letters **3**, 137 (1959).

<sup>15</sup> W. A. Harrison, Phys. Rev. **118**, 1190 (1960).

<sup>16</sup> E. Fawcett, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 166.

<sup>17</sup> T. W. Moore (private communication).

but as yet they have not been calculated convincingly for real metals.

The problem of how correlations should be handled is quite complex and as yet incompletely understood. One important point that can be made, however, is that the effects of the electron-electron interactions enter in differently in different physical processes. Kohn<sup>18</sup> has shown, for example, that for the case of an electron gas the interactions do not alter the cyclotron frequency (and hence the cyclotron mass) from its free-electron value. On the other hand, from Gell-Mann's<sup>19</sup> work we know that they do contribute to the specific heat of an electron gas. In view of this, it would seem more appropriate not to include many-electron corrections in a band calculation like the present one.<sup>20</sup> The contribution to a specific property arising from the electron-electron—as well as electron-phonon—interactions would then be considered separately for that particular property (when the correct approach is known).

In his paper, Heine included a correlation and exchange correction based on the first-order Bohm-Pines theory. Even for those properties for which this theory appears most appropriate like the specific heat, the first-order treatment is quantitatively incorrect as in that case it leads to sizable correction of the wrong sign. Also, as mentioned in Sec. III, the second-order corrections to  $E(\mathbf{k})$  are not small for all  $\mathbf{k}$ , and this leads to doubts about the convergence of the higher order terms.

In a subsequent paper the present work will be extended. There we will investigate the Fermi surface and determine some of the effective masses of interest for the band structure discussed in this work.

Finally, we should note that the primary assumption in the construction of the potential—aside from the validity of the individual-particle model—has been shown to be quite consistent with the results of the calculation. This assumption pertained to the free-electron nature of the energy bands and the charge density outside the core region.

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<sup>18</sup> W. Kohn, Phys. Rev. **123**, 1242 (1961).

<sup>19</sup> M. Gell-Mann, Phys. Rev. **106**, 369 (1957).

<sup>20</sup> W. A. Harrison, reference 16, p. 28.