

where  $R$  is a unitary time independent operator which has the property

$$R^{-1}HR = R^\dagger HR = H^*, \quad (\text{A5})$$

Eq. (A2) becomes equivalent to (A3) and thus to (A1). We see then that the condition for invariance under time reversal is the existence of the operator  $R$ .

We now apply the results just derived to our problem. Specifically, we introduce "time reversed" states according to the definition

$$\Phi_{-b} \equiv R\Phi_b^*, \quad (\text{A6})$$

where  $\Phi_{-b}$  is the time reversed state corresponding to  $\Phi_b$ . [For the simple case of a particle without spin,  $R$  is unity and if  $\Phi_b = \exp(i\mathbf{k} \cdot \mathbf{r})$ ,  $\Phi_{-b} = \exp(-i\mathbf{k} \cdot \mathbf{r})$  which evidently corresponds to a wave traveling in the opposite direction and hence with reversed velocity.] From our explicit equation for  $\Omega^{(\pm)}$ , namely,

$$\Omega^{(+)} = 1 + \frac{1}{E + i\eta - H} V, \quad (\text{A7})$$

one finds using (A5)

$$R^\dagger \Omega^{(+)} R = 1 + \frac{1}{E + i\eta - H^*} V^* = \Omega^{(-)T}, \quad (\text{A8})$$

where we have assumed  $H_0$  and  $V$  are hermitian and used the

result

$$\Omega^{(-)} = 1 + V \frac{1}{E + i\eta - H}. \quad (\text{A9})$$

This proves the remark made in the text following Eq. (9). Written more explicitly, Eq. (A8) furnishes the information

$$(\Phi_b, \Omega^{(-)}\Phi_a) = (\Phi_{-a}, \Omega^{(+)}\Phi_{-b}). \quad (\text{A10})$$

As a further illustration of the interconnection between the various operators  $T^{(\pm)}$  and state vectors  $\Psi^{(\pm)}$  we note the following results:

$$\begin{aligned} \Psi_{-a}^{(+)} &= R\Psi_a^{(+)*} = \Omega^{(-)\dagger}\Phi_{-a}, \\ \Psi_{-b}^{(-)} &= R\Psi_b^{(-)*} = \Omega^{(+)}\Phi_{-b}. \end{aligned} \quad (\text{A11})$$

These express the not unexpected interchange of incoming and outgoing scattered waves. With (A11) it is easy to show that the usual form of the reciprocity law<sup>4</sup>

$$(\Psi_b^{(-)}, V\Phi_a) = (\Phi_b, V\Psi_a^{(+)}) \quad (\text{A12})$$

takes on the form

$$(\Phi_{-a}, V\Omega^{(+)}\Phi_{-b}) = (\Phi_b, V\Omega^{(+)}\Phi_a) \quad (\text{A13})$$

or, in terms of  $T^{(\pm)} = V\Omega^{(\pm)}$ ,

$$T_{-a, -b}^{(+)} = T_{b, a}^{(+)}. \quad (\text{A14})$$

## An Application of the Cellular Method to Silicon\*

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The calculations of Kimball and Mullaney applying the cellular method to elemental silicon are extended to a higher approximation. Although the energy gap is decreased through use of a larger number of harmonics, the values obtained are still much higher than that given by experiment. The proposal of Pearson, Haynes, and Shockley that the highest point of the filled band and the lowest point of the conduction band do not occur at the center of the zone may have a bearing on the results, since the calculations reported here are performed for zero wave number. The effective mass of the conduction electrons is determined under the assumption that the lowest point lies at the center of the zone.

### INTRODUCTION

THE pure silicon crystal has the diamond type lattice and an experimentally known excitation energy as a semiconductor of 1.12 ev.<sup>1</sup> Kimball<sup>2</sup> obtained a solution for the band structure of diamond by use of the cellular method and Mullaney<sup>3</sup> adapted the diamond solution to silicon. Essentially the same method is used in part I of this paper to determine the lowest energy limit of the conduction band and the highest limit of the filled band, each for several possible values of the lattice spacing (under the assumption that the band limits occur at the center of the brillouin zone in a reduced scheme). The principal difference from previous

work is in the choice of boundary conditions to be used in the fitting. In part II the functions obtained in part I are used to determine the effective mass for the conduction electrons.

The work reported here was performed in 1949 when it seemed likely that the top of the filled band and the bottom of the empty band did occur at the center of the brillouin zone. Pearson, Haynes, and Shockley have presented evidence<sup>4</sup> that these points may actually lie elsewhere in the brillouin zone. In spite of this, the calculations seem worth presenting briefly for their general value in connection with the properties of silicon.

### I. THE BAND LIMITS

The total one electron eigenfunction may be expressed as<sup>5</sup>

$$\psi = \sum_l A_l [\sum_m C_{lm} Y_l^m(\phi, \theta)] R_l(E, r), \quad (1)$$

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<sup>1</sup> H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), p. 64.

<sup>2</sup> G. E. Kimball, *J. Chem. Phys.* **3**, 560 (1935).

<sup>3</sup> J. F. Mullaney, *Phys. Rev.* **66**, 326 (1944).

<sup>4</sup> Pearson, Haynes, and Shockley, *Phys. Rev.* **78**, 295 (1950).

<sup>5</sup> F. C. VonderLage and H. A. Bethe, *Phys. Rev.* **71**, 612 (1947).

where the  $Y_l^m$  are surface spherical harmonics and the  $R_l$  are solutions of the radial Schrödinger equation for the free silicon atom. If the  $C_{lm}$  are obtained explicitly leaving the  $A_l$  undetermined, the total  $\psi$  may be fitted at the surface of the lattice cell for only a particular value of the energy, which appears as a parameter in the  $R_l$ . The angular parts may be constructed by noting that in the work of both Kimball and Mullaney the following conclusions are reached:

- (1) At the bottom of the conduction band the wave functions are  $s$ -type about each nucleus and change sign upon inversion through the center of symmetry midway between adjacent nuclei.
- (2) At the top of the filled band they are correspondingly  $p$ -type and even.

Thus it would be expected,<sup>6</sup> if these conclusions are actually acceptable, that the characteristic polynomials for the conduction band belong to the  $\Gamma_1$  representation of the tetrahedral rotation group which expresses the symmetry of the silicon lattice, while the polynomials for the filled band would belong to the  $\Gamma_4$  representation. Since the contribution of the higher harmonics is presumably small, only the first three characteristic polynomials were used in the total  $\psi$  for the conduction band, and only the first two for the filled band; these polynomials are listed below:

$$\Gamma_1: 1, \quad xyz, \quad x^2y^2+y^2z^2+x^2z^2-\frac{1}{3}(x^4+y^4+z^4); \quad (2a)$$

$$\Gamma_4: x, \quad yz. \quad (2b)$$

In order to fit the total wave functions of (1) so that they are continuous and have the periodicity and symmetry of the lattice, the appropriate number of boundary conditions must be chosen on the surface of the unit cell of the lattice. Figure 1 shows the polyhedron formed by passing bisecting planes perpendicularly through the lines joining a given silicon atom to its nearest and next-nearest neighbors. Since there are two atoms per unit cell in the silicon crystal, the surface of the unit cell is made up of two such polyhedra coinciding in a hexagonal face but rotated  $60^\circ$  with respect to each other about the line joining the two atoms of the unit cell. At equivalent points of the two polyhedra of the unit cell the  $\Gamma_1$  wave function is equal-valued but has opposite signs in the two polyhedra; the  $\Gamma_4$  wave functions for the two polyhedra pass into each other upon inversion in the midpoint of the common hexagonal face. The boundary conditions are applied at points of special symmetry, "a," "b,"

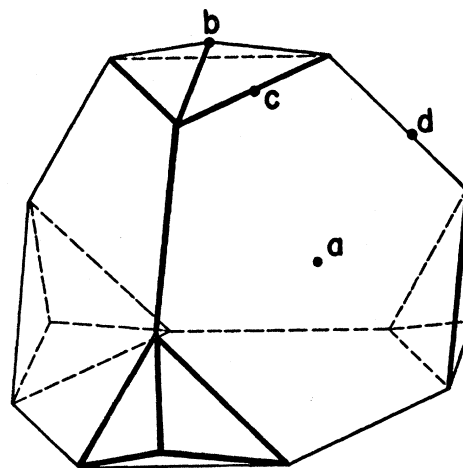


FIG. 1. The cellular polyhedron for silicon.

"c," and "d" of Fig. 1. Point "a" lies midway between two nearest neighbors at an experimentally determined distance of 2.22 Bohr radii from each atom of the unit cell. At "a" the total wave function with the symmetry of  $\Gamma_1$  should have a node, while the total wave function belonging to  $\Gamma_4$  should have a vanishing radial derivative. The vertices of four translationally equivalent polyhedra coincide at "b"; at this point the  $\Gamma_1$  function may be expected to have a vanishing radial derivative, while the  $\Gamma_4$  function itself should be zero. The third boundary condition needed for the  $\Gamma_1$  wave function is obtained by noting that points "c" and "d" exchange symmetries on passage between the two polyhedra, so that the wave function at point "c" must be the negative of that at point "d." The following, then, are the boundary condition equations:

$$\Gamma_1: \psi(a)=0, \quad (d\psi/dr)_{(b)}=0, \quad \psi(c)=-\psi(d). \quad (3)$$

$$\Gamma_4: (d\psi/dr)_{(a)}=0, \quad \psi(b)=0. \quad (4)$$

When the  $\psi$ 's of Eq. (1) containing the polynomials of Eq. (2) are substituted into Eqs. (3) and (4) there result two systems of equations for the  $A_l$  for the two cases,  $\Gamma_1$  and  $\Gamma_4$ .<sup>7</sup> The determinantal equations which are the conditions for the solubility of the equations in the  $A_l$  are satisfied only when the  $R_l$  going with a particular energy are used. The eigenenergy was obtained for several lattice spacings with the results given in Table I.

Thus the energy gap as calculated for the center of the zone is much greater than 1.12 eV, the experimental value; however, as mentioned above, recent evidence<sup>4</sup> indicates that the smallest band separation may correspond to other than zero wave number.

## II. THE EFFECTIVE MASS

The one-electron wave functions which were fitted to the silicon lattice in the preceding work may be used in

<sup>7</sup> The values of the radial wave functions  $R_l$  were obtained directly from reference 3 or by numerical integration using the effective potential given in reference 3.

TABLE I. Band-limit energies and excitation energies.

Internuclear separation (Bohr radii)	$E$ (conduction band) (Rydberg units)	$E$ (filled band) (Rydberg units)	Excitation energy (electron volts)
4.44	0.314	-0.424	9.983
4.66	0.159	...	...
4.88	0.057	-0.465	7.068
5.48	-0.091	-0.448	4.834

<sup>6</sup> D. H. Ewing and F. Seitz, Phys. Rev. 50, 760 (1936).

TABLE II. The ratio  $m^*/m$ .

Internuclear separation	$m^*/m$
4.44	0.223
4.80	0.186
5.00	0.164

a determination of the effective mass of an electron occupying a level near the bottom of the conduction band.<sup>8</sup> We take the one-electron wave function going with wave number  $\mathbf{k}$  in the form

$$\psi_k = \chi_k e^{i(\mathbf{k}\cdot\mathbf{r})}, \quad (5)$$

as usual, so that  $\psi$  of Eq. (1) is given by

$$\psi = \chi_0. \quad (6)$$

The differential equation satisfied by  $\chi_k$  which is obtained by substituting the form (5) into the Schrödinger equation satisfied by  $\psi_k$ , is

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\chi_k - \frac{i\hbar^2}{m}(\mathbf{k}\cdot\nabla\chi_k) + V\chi_k \\ = \left(E_k - \frac{\hbar^2k^2}{2m}\right)\chi_k \cong E_0\chi_k. \end{aligned} \quad (7)$$

For small  $k = |\mathbf{k}|$  we assume

$$\chi_k = \chi_0 + ik\chi', \quad (8)$$

where  $ik\chi'$  is a small perturbation on  $\chi_0$ , and substitute into Eq. (7), obtaining (with the neglect of second-order terms)

$$-(\hbar^2/2m)\nabla^2\chi' - (\hbar^2/km)(k\cdot\nabla\chi_0) + V\chi' = E_0\chi'. \quad (9)$$

The total solution of (9) may be taken in the form

$$\chi' = -[(\mathbf{k}\cdot\mathbf{r})/k]\chi_0 + \chi'', \quad (10)$$

where  $\chi''$  satisfies

$$-(\hbar^2/2m)\nabla^2\chi'' + V\chi'' = E_0\chi''. \quad (11)$$

Since  $\chi'$  and therefore  $\chi''$ , have the symmetry of  $\nabla\chi_0$ , i.e., the  $\Gamma_4$  symmetry, an expansion of the type of Eq. (1) may be made for  $\chi''$  using the radial functions going with  $E_0$  and the angular harmonics given in (2b). The boundary conditions of Eq. (4) may be applied to  $\chi''$  to determine the coefficients of the two terms in the

<sup>8</sup> This work follows that of J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

expansion. With this definite form for  $\chi''$ ,  $\chi'$  is completely specified by Eq. (10) and, thus,  $\chi_k$  is completely specified by Eq. (8). The energy  $E_k$  going with  $\chi_k$  may now be obtained from

$$E_k = c^2 \int \chi_k^* e^{-i(\mathbf{k}\cdot\mathbf{r})} \left( -\frac{\hbar^2}{2m}\nabla^2 + V \right) \chi_k e^{i(\mathbf{k}\cdot\mathbf{r})} d\tau, \quad (12)$$

where the following normalization condition is to be imposed on  $\chi_k$ :

$$c^2 \int \chi_k^* \chi_k d\tau = 1. \quad (13)$$

The integrals in both (12) and (13) are to be taken over the unit cell. When the explicit form for  $\chi_k$  along with the differential equations satisfied by  $\chi_0$ ,  $\chi'$ , and  $\chi''$  are used in Eqs. (12) and (13) (and higher order terms neglected) the following form for  $E_k$  results:

$$E_k = E_0 + \frac{\hbar^2k^2}{2m} + \frac{c^2\hbar^2k^2}{m} \int \chi_0 \frac{\partial\chi'}{\partial x} d\tau. \quad (14)$$

Here the  $\mathbf{k}$  vector has been arbitrarily chosen in the  $x$  direction for numerical computation, since, to the approximation used here, the direction chosen at the center of the zone is not significant. If  $E_k$  is expressed in the usual form,

$$E_k = E_0 + \hbar^2k^2/2m^*, \quad (15)$$

then  $m^*$ , the effective electron mass, takes the form

$$m^* = m \left[ 1 + \frac{2 \int \chi_0 (\partial\chi'/\partial x) d\tau}{\int \chi_0^2 d\tau + k^2 \int \chi''^2 d\tau} \right]^{-1}, \quad (16)$$

with all integrals, again, to be taken over the unit cell.

The integrals in (16) were performed numerically for three values of the lattice spacing with the results for the ratio of  $m^*$  to  $m$  given in Table II.

A value of  $m^*/m$  of 0.67 has been reported by Pearson and Bardeen,<sup>9</sup> but it is not certain at this time that the calculated values have immediate bearing on the values obtained by Pearson and Bardeen.

<sup>9</sup> G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).