

## The Electronic Structure of Diamond

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## The Electronic Structure of Diamond

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The method of Wigner, Seitz and Slater has been applied to the determination of the electronic structure of diamond. It is found that the energy levels of the carbon atom are broadened into bands similar to the energy bands in metals. The  $2s$  level of the atom splits into two bands, and the  $2p$  level into six bands. The two  $2s$  bands are completely

filled by electrons and the two lowest of the  $2p$  bands. The lowest unfilled band has a much higher energy than the highest filled band. The lack of electrical conductivity is explained and other properties of the diamond are discussed.

ALTHOUGH Hund<sup>1</sup> has given a very good qualitative discussion of the properties of crystals of all types in relation to their electronic structure, quantitative discussion of the electronic eigenfunctions in crystals has been confined to metals. Three methods have been devised to treat these problems. In the free electron model, it is assumed that to a first approximation the eigenfunctions are those of free electrons, and the potentials of the nuclei and other electrons are treated as a perturbation. In the method of Bloch, the electrons are assumed as a first approximation to be in states represented by linear combinations of atomic eigenfunctions. Finally, in the method of Wigner and Seitz, the crystal is divided into cells of approximately spherical shape. Eigenfunctions are then found which satisfy Schrödinger's equation within these cells and which are joined smoothly at the cell boundaries.<sup>2</sup>

In this paper the method of Wigner and Seitz, as extended by Slater, has been applied to diamond, chosen as the most typical nonmetallic crystal, with the object of explaining the characteristic differences between metals and non-metals.

The crystal structure of diamond, as determined by W. H. and W. L. Bragg,<sup>3</sup> is face-centered cubic with two atoms in the unit cell. If we locate one atom at the origin of a Cartesian coordinate system, and the second atom of the cell at  $(a, a, a)$ , the whole lattice may be gener-

ated by translating these atoms by vectors of the form  $n_1\mathbf{v}_1 + n_2\mathbf{v}_2 + n_3\mathbf{v}_3$ , where the components of  $\mathbf{v}_1$  are  $0, 2a, 2a$ , those of  $\mathbf{v}_2$  are  $2a, 0, 2a$ , and those of  $\mathbf{v}_3$  are  $2a, 2a, 0$ , while  $n_1, n_2$ , and  $n_3$  are arbitrary integers. Each atom of the lattice is surrounded by four nearest neighbors at a distance  $2R = \sqrt{3} a$ . It is found experimentally that  $a = 0.89\text{\AA} = 1.69$  Bohr radii.

In order to apply the method of Wigner and Seitz it is necessary to surround each atom by a cell formed by planes bisecting the lines joining the atom to its neighbors. In the diamond structure the planes bisecting the lines joining any atom to its four nearest neighbors form a regular tetrahedron. The twelve planes bisecting the lines to the next nearest neighbors cut off the corners of this tetrahedron, leaving a 16-sided solid, illustrated in Fig. 1. The cells surrounding the two atoms of the unit cell of the crystal are identical, but are oppositely oriented.

To join the eigenfunctions at all 16 faces of these cells is so complicated that it is impracticable. It was therefore decided to fit the eigenfunctions so that the value and normal derivative would be continuous at the four points midway between the atom and its nearest neighbors, that is, at the centers of the hexagonal faces of the cell.

Since there are two atoms in the unit cells of the crystal this joining must be carried out for two Wigner-Seitz cells simultaneously. If we take as our two cells those surrounding the atoms at  $(0, 0, 0)$  and  $(a, a, a)$  the joining points for the first cell are  $P_1 = (a/2, a/2, a/2)$ ,  $P_2 = (a/2, -a/2, -a/2)$ ,  $P_3 = (-a/2, a/2, -a/2)$ , and  $P_4 = (-a/2, -a/2, a/2)$ . For the second cell the joining points are  $P_5 = (a/2, a/2, a/2)$ ,  $P_6 = (a/2, 3a/2, 3a/2)$ ,  $P_7 = (3a/2, a/2, 3a/2)$ , and  $P_8 = (3a/2, 3a/2, a/2)$ . ( $P_1$  and  $P_5$  coincide of course, but it is convenient

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<sup>1</sup> Papers and Discussions of the Int. Conf. Phys., London, 1934. Vol. II, p. 36 (Published by the Physical Society, London).

<sup>2</sup> These methods are described in detail and with complete literature references in a review by J. C. Slater, *Rev. Mod. Phys.* **6**, 210 (1934).

<sup>3</sup> Bragg, *Proc. Roy. Soc. A* **89**, 277 (1913).

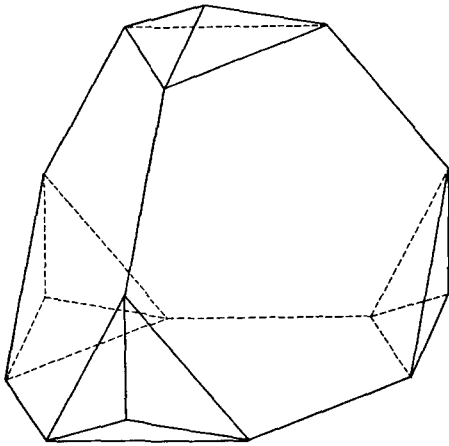


FIG. 1. The Wigner-Seitz cell for diamond.

to have different notations when regarding the point as in the first or second cell.)

The requirement that the eigenfunction have the same value at  $P_1$  as at  $P_5$  involves one condition on the eigenfunction. Since  $P_5$  is translated from  $P_2$  by the lattice vector  $\mathbf{v}_1$ , the usual Bloch condition requires that the value of the eigenfunction at  $P_5$  be the value at  $P_2$  multiplied by a factor  $\exp i\mathbf{k} \cdot \mathbf{v}_1$ , where  $\mathbf{k}$  is an arbitrary vector determining the wavelength and direction of the electron wave through the crystal. Similarly the value of the eigenfunction at  $P_7$  must be the value at  $P_3$  multiplied by  $\exp i\mathbf{k} \cdot \mathbf{v}_2$  and the value at  $P_8$  must be the value at  $P_4$  multiplied by  $\exp i\mathbf{k} \cdot \mathbf{v}_3$ . These four conditions, plus the four similar conditions on the derivative of the eigenfunction, make eight conditions in all which

must be satisfied by the eigenfunctions in the two cells.

If we choose eight eigenfunctions  $\psi_1, \psi_2, \dots, \psi_8$ , and assume that our final eigenfunction is a linear combination of the form

$$\Psi = iA\psi_1 + iB\psi_2 + iC\psi_3 + iD\psi_4 + E\psi_5 + F\psi_6 + G\psi_7 + H\psi_8,$$

where  $A, B, \dots, H$  are constants, then the eight conditions are just sufficient to determine the eight constants. (The factor  $i$  has been introduced for later convenience.) The eight eigenfunctions chosen were constructed from an  $s$  eigenfunction and three  $p$  eigenfunctions for each of the two atoms. The exact functions are shown in Table I. In this table  $S(r)$  is the  $s$

TABLE I.

EIGEN-FUNCTION	VALUE IN CELL ABOUT (0, 0, 0)	VALUE IN CELL ABOUT (a, a, a)
$\psi_1$	$S(r)$	$-S(r')$
$\psi_2$	$\sqrt{3}(x/r)P(r)$	$\sqrt{3}(x'/r')P(r')$
$\psi_3$	$\sqrt{3}(y/r)P(r)$	$\sqrt{3}(y'/r')P(r')$
$\psi_4$	$\sqrt{3}(z/r)P(r)$	$\sqrt{3}(z'/r')P(r')$
$\psi_5$	$S(r)$	$S(r')$
$\psi_6$	$\sqrt{3}(x/r)P(r)$	$-\sqrt{3}(x'/r')P(r')$
$\psi_7$	$\sqrt{3}(y/r)P(r)$	$-\sqrt{3}(y'/r')P(r')$
$\psi_8$	$\sqrt{3}(z/r)P(r)$	$-\sqrt{3}(z'/r')P(r')$

eigenfunction and  $P(r)$  the radial part of the  $p$  eigenfunction of an electron of energy  $E$  in the field of an ionized carbon atom.  $x, y, z$  are Cartesian coordinates with origin at (0, 0, 0) and  $r$  is the distance from (0, 0, 0).  $x', y', z'$  and  $r'$  have corresponding significance with respect to the point (a, a, a).

The eight equations of continuity of value and derivative may then be written in the form<sup>4</sup>

$$\begin{aligned} sA + p(B + C + D) &= 0 & (1a) \\ sA + p(-B - C - D) + KsE + Kp(F - G - H) &= 0 & (1b) \\ sA + p(-B + C - D) + LsE + Lp(-F + G - H) &= 0 & (1c) \\ sA + p(-B - C + D) + MsE + Mp(-F - G + H) &= 0 & (1d) \\ s'E + p'(F + G + H) &= 0 & (1e) \\ -Ks'A - Kp'(B - C - D) + s'E + p'(F - G - H) &= 0 & (1f) \\ -Ls'A - Lp'(-B + C - D) + s'E + p'(-F + G - H) &= 0 & (1g) \\ -Ms'A - Mp'(-B - C + D) + s'E + p'(-F - G + H) &= 0 & (1h) \end{aligned}$$

where  $s = S(R)$ ,  $s' = (dS/dr)_{r=R}$ ,  $p = P(R)$ ,  $p' = (dP/dr)_{r=R}$ .  $K, L$  and  $M$  are defined by  $K = \tan(\mathbf{k} \cdot \mathbf{v}_1/2)$ ,  $L = \tan(\mathbf{k} \cdot \mathbf{v}_2/2)$  and  $M = \tan(\mathbf{k} \cdot \mathbf{v}_3/2)$ .

In order that  $A, B, \dots, H$  shall not all vanish it is necessary that the determinant of the coefficients vanish. The vanishing of this determinant

gives one relation between  $K, L, M$  and hence between the components of  $\mathbf{k}$ , since  $s, s', p$  and  $p'$  are fixed if  $E$  and  $a$  are fixed. Thus if the direction of  $\mathbf{k}$  is chosen, its magnitude is determined.

<sup>4</sup> The derivation of these equations is exactly similar to the reduction used by Slater, Phys. Rev. **45**, 796 (1934).

Unfortunately it is not feasible to solve this determinantal equation in general.

If, however, the direction of  $\mathbf{k}$  is chosen to lie in the plane  $x=y$  it becomes possible to reduce Eqs. (1). If  $\mathbf{k}$  lies in this plane,  $K=L$ . Placing

$L=K$  in Eqs. (1), add and subtract Eqs. (1b) and (1c), and Eqs. (1f) and (1g). Letting  $B+C=U$ ,  $B-C=V$ ,  $F+G=X$ , and  $F-G=Y$  Eqs. (1) become

$$\begin{aligned} sA + pU + pD &= 0 & (2a) \\ sA - pD + KsE &- KpH = 0 & (2b) \\ sA - pU + pD + MsE - MpX + MpH &= 0 & (2c) \\ -Ks'A + Kp'D + s'E &- p'H = 0 & (2d) \\ -Ms'A + Mp'U - Mp'D + s'E - p'X + p'H &= 0 & (2e) \\ s'E + p'X + p'H &= 0 & (2f) \\ pV + KpY &= 0 & (3a) \\ -Kp'V + p'Y &= 0. & (3b) \end{aligned}$$

Unless  $p$  or  $p'=0$  Eqs. (3) require  $V=Y=0$  for all real  $K$ . In order that  $A, U, D, E, X$  and  $H$  do not all vanish we must have

$$\begin{vmatrix} s & p & p & 0 & 0 & 0 \\ s & 0 & -p & Ks & 0 & -Kp \\ s & -p & p & Ms & -Mp & Mp \\ -Ks' & 0 & Kp' & s' & 0 & -p' \\ -Ms' & Mp' & -Mp' & s' & -p' & p' \\ 0 & 0 & 0 & s' & p' & p' \end{vmatrix} = 0. \quad (4)$$

If we let  $\mu = sp'/s'p$  this equation reduces to

$$(\mu+3)(3\mu+1)K^2M^2 + 4(\mu+1)^2K^2 - 4(\mu-1)^2KM + (\mu+3)(3\mu+1)M^2 + 16\mu = 0. \quad (5)$$

Finally if we let  $\omega = (\mu^2+1)/\mu$  we may put this equation into the form

$$\omega = \frac{-(10K^2M^2 + 8K^2 + 8KM + 10M^2 + 16)}{3K^2M^2 + 4K^2 - 4KM + 3M^2}. \quad (6)$$

Thus  $\omega$  can be evaluated directly from  $\mathbf{k}$ . By means of a plot of  $\omega$  against the energy  $E$ , the value of  $E$  can therefore be found from  $\mathbf{k}$ .

Construction of such a plot of  $\omega$  against  $E$  involves the determination of  $s, s', p$  and  $p'$  for a number of values of  $E$ . These values were computed by numerical integration of the radial part of Schrödinger's equation. As a first approximation to the potential field inside the cell, the potential calculated from the eigenfunctions of the free carbon atom calculated by Torrance<sup>5</sup> was used. From the results of a series of numerical integrations  $s, s', p$  and  $p'$  were found as a function of  $E$  for a range of values of  $a$ . In Fig. 2 the results are shown in a plot of  $E$  against  $R$ . The equation of curve I is  $s'=0$ ; curve II,  $s/s'$

$+p/p'=0$ ; curve III,  $s=0$ ; curve IV,  $p'=0$ ; curve V,  $s/s'+p/p'=0$ ; and curve VI,  $p=0$ .

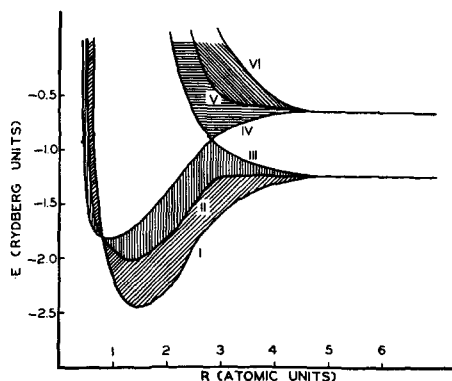
When  $E$  is found as a function of  $\mathbf{k}$  using Eq. (6) it is found that to each value of  $\mathbf{k}$  there correspond four values of  $E$ . One of these values lies in the diagonally shaded region bounded by curves I and II in Fig. 2; the second in the vertically shaded region bounded by curves II, III and IV; the third in the horizontally shaded region bounded by curves III, IV and V; and the fourth in the diagonally shaded region between curves V and VI. Besides these values of  $E$  it is found that Eqs. (2) are satisfied by any value of  $\mathbf{k}$  if either  $p=0$  or  $p'=0$  and Eqs. (3) are also satisfied for any  $\mathbf{k}$  if  $p=0$  or  $p'=0$ .

Thus for any value of  $\mathbf{k}$  there are eight possible eigenfunctions, two pairs being degenerate. Fig. 2 shows that as the internuclear distance is increased the two lowest bands of energy levels go over into the  $2s$  level of the carbon atom, while the other six bands go over into the  $2p$  level. Now at infinite separation the  $2s$  level contains two electrons, so that it is reasonable to suppose that each band will be filled by one electron per atom. A calculation of the type given by Slater<sup>6</sup> confirms this argument. Since there are four electrons per atom in carbon (neglecting the  $1s$  electrons) the normal state of the crystal will have the two  $2s$  bands filled and the two lowest  $2p$  bands, i.e., the two degenerate bands following curve IV in Fig. 2. The energies of all these bands are lowest in the neighborhood of the observed internuclear distance ( $R=1.46$  Bohr radii).

While the calculations made with the atomic potential field are probably reasonably accurate

<sup>5</sup> Torrance, Phys. Rev. **46**, 388 (1934).

<sup>6</sup> Slater, Rev. Mod. Phys. **6**, 276 (1934).



for large internuclear distances, the crowding of electrons toward the nucleus when the interatomic distance is small undoubtedly produces serious changes in the potential field. For this reason a second approximation to the field was made for the particular distance  $R=1.44$ . In this calculation, however, a difficulty arises with the additive constant occurring in the potential. A number of choices are possible for this constant. The usual choice is to fix this constant in such a way that the energy levels of the inner shells of electrons are not changed. In this case, however, this procedure would lead to too low a value for the total energy, for there are four electrons being crowded into a nucleus whose charge is only six electronic units. A rough calculation shows that the effective nuclear charge may be changed by as much as two units, or 33 percent, hardly a negligible change.

A second way in which the constant might be fixed would be to assume that the field due to the crystal outside the cell in question is zero, so that the potential at the surface of the cell is  $e/R$ . The energy obtained by the first choice is too low, that from the second choice is too high. It seems impossible to determine a reasonable choice of this constant without a complete evaluation of the energy in the way outlined by Slater.<sup>7</sup>

The eigenfunctions calculated from the second approximation to the potential lead to the rela-

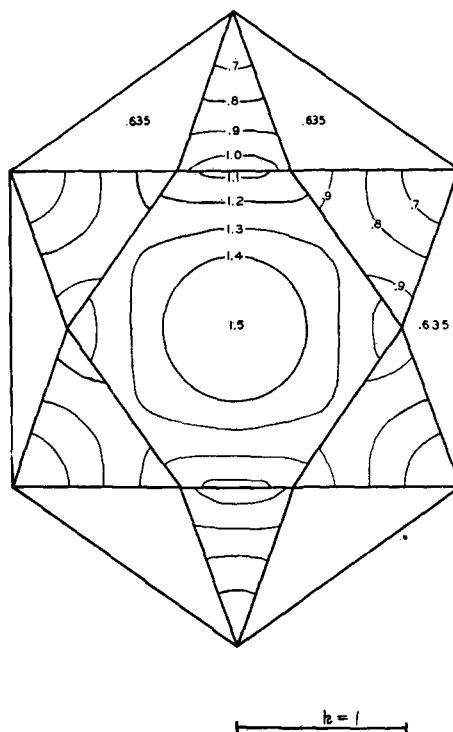


FIG. 3. Energy as a function of  $k$  for values of  $k$  lying in the plane  $x=y$ . The contours give  $-E$  in Rydberg units.

For the eigenfunctions of these bands the energy has the same value for all values of  $k$ .

Although not very much of a quantitative nature can be concluded from these results, the essential differences between diamond and the metals are apparent. In a metal there is always an energy band which is not completely filled. As the various workers on metals have shown, the electrical conductivity is a direct consequence of this fact. In the diamond the low energy bands are all completely filled, and a large amount of energy would be necessary to promote an electron to an unfilled band. Now in each band, for every electron wave traveling in one direction there is a second wave of the same energy traveling in the opposite direction. The net result is that a filled band can produce no flow of charge. Hence it follows that the diamond is a non-conductor.

Some conclusions can be drawn with respect to the absorption spectrum. At the normal internuclear distance the curve III has risen to such a high energy that transitions of electrons from the filled bands to the band lying above it would take more energy than the ionization potential of the normal carbon atom. It is almost certain that some band arising from the  $3d$  level of the carbon atom will have a lower energy. If ultraviolet light is absorbed by diamond it is most probable that the transition which actually takes place is one to

such a level. Peter<sup>8</sup> has measured the absorption coefficient and refractive index of diamond down to 2260Å. No absorption bands were found, but extrapolation of the dispersion curve indicates an absorption band in the neighborhood of 1750Å, corresponding to an excitation energy of about 7 electron volts. This value seems too low for a transition to a  $2p$  band, and therefore is almost certainly evidence of a low  $3d$  band.

An interesting feature of the eigenfunctions of the diamond is the change in character of the eigenfunctions of the second lowest band as the internuclear distance is decreased. For large separations the eigenfunctions of this band are  $s$ -like in character, but after the point of intersection of curves III and IV (Fig. 2) has been passed the eigenfunctions have essentially the character of  $p$  functions. This change in character is essentially the promotion which Heitler and London have postulated to account for the quadrivalence of carbon. There is, however, no sign of the combination of  $s$  and  $p$  eigenfunctions into the "tetrahedral" eigenfunctions postulated by Slater and Pauling to account for the phenomena of directed valence observed in carbon.

The author wishes to express his deep appreciation to Professor J. C. Slater for his assistance and discussions of this problem.

<sup>8</sup> Peter, *Zeits. f. Physik* **15**, 358 (1923).

## Electronic Structures of Molecules

### X. Aldehydes, Ketones and Related Molecules

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Electron configurations for the normal states of  $H_2CO$ ,  $CH_3HCO$ ,  $Cl_2CO$  are explicitly given, also for the low excited states of  $H_2CO$ . The structures, ionization potentials, and longest wavelength electronic band spectra of these and other related or analogous molecules (saturated aldehydes, ketones, thioaldehydes, thioketones, etc.) are interpreted in relation to these configurations. In particular it is shown that the minimum ionization potential of  $>C=O$  or  $>C=S$  corresponds to removal of a nonbonding  $2p$  electron from the O atom or a nonbonding  $3p$  from the S atom, unless the groups attached to the C contain other unusually easily ionized electrons. Similarly, the longest wavelength band system, commonly attributed

to the  $C=O$  (or  $C=S$ ) double bond, corresponds to excitation of the nonbonding  $2p$  or  $3p$ s to an excited orbital which is largely but probably not quite wholly localized in the  $C=O$  or  $C=S$  bond, and which has  $C \leftrightarrow O$  or  $C \leftrightarrow S$  antibonding power, i.e., loosens the bond somewhat. This excitation process is responsible for color in the  $>C=S$  compounds. The  $C=O$  (or  $C=S$ ) bond is a true double bond in the sense that the binding is effected essentially by two pairs of  $C-O$  (or  $C-S$ ) bonding electrons. The  $C=O$  bond is essentially the same also in saturated monobasic acids  $RCOOH$  or at least in their esters.