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ON THE COHESION OF COVALENT STRUCTURES OF ELEMENTS IN CONDENSED PHASES. I. — COHESION OF $\sigma$ AND $\pi$ BANDS IN A SIMPLE HÜCKEL APPROXIMATION

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Résumé. — La cohésion des structures covalentes est étudiée systématiquement dans une approximation de Hückel (LCAO) simplifiée, qui ne considère qu'un type d'intégrale de transfert interatomique pour chaque liaison ($\sigma$ ou $\pi$). Les structures à plans ou à chaînes avec une ou deux liaisons $\sigma$ coupées par atome sont comparées aux structures $sp^n$ saturées ou conjuguées. Celles-ci sont aussi comparées aux structures compactes métalliques $sp$ et aux structures covalentes $p$. La description générale est en accord qualitatif avec l'expérience ; mais elle conduit à des énergies de cohésion trop élevées ; et la stabilité relative des structures à plans et à chaînes des éléments tétra, penta et hexavalents est trop faible.

Abstract. — The cohesion of covalent structures is systematically studied in a simplified Hückel (LCAO) approximation which only allows for one type of interatomic transfer integral for each ($\sigma$ or $\pi$) bond. Layers or chains structures with one or two broken $\sigma$ bonds per atom are compared with saturated or conjugated $sp^n$ structures. These are also compared with compact metallic $sp$ and with covalent $p$ structures. The overall description is in qualitative agreement with experiment ; but cohesive energies are too large and the relative stability of layer and chain structures of tetra, penta and hexavalent elements is too small.

1. Introduction. — Elements somewhat on the right of the $sp$ series (with 3 to 6 valence electrons per atom) tend to form more or less covalent and continuous structures in their condensed (crystalline, amorphous or liquid) phases. These are characterized for each atom by a small number of interatomic bonds with its nearest neighbours, at fairly definite angles from each other [1].

The most typical of such bonds are the $\sigma$ and $\pi$ bonds formed by tetravalent atoms such as carbon in saturated or conjugated structures (Fig. 1). Thus each atom has

— four equidistant neighbours in a tetrahedral coordination forming four $\sigma$ bonds in a 3 dimensional phase ;
— or three equidistant neighbours in a triangular coordination, forming 3 $\sigma$ bonds and 3 $\pi$ resonant bonds in a 2 dimensional phase ;
— or two equidistant neighbours forming 2 $\sigma$ bonds and 4 $\pi$ resonant bonds in a one dimensional phase.

In the last case, long enough chains should show a dimerization (Fig. 2a) which would localize somewhat the $\pi$ bonding. We will not discuss this distortion here. Similarly, two and three dimensional phases can exist which respect the local topology of bonding

Fig. 1. — Three types of $\sigma$ and resonant $\pi$ bondings discussed.

Fig. 2. — Two types of distortions neglected.
but destroy the long range order at the expense of a slight distortion of the bonds, in their lengths or relative angles. We shall consider such amorphous structures, but again neglect the distortions of the bonds, which should add here a small elastic (negative) contribution to cohesion.

We shall only consider large (macroscopic) aggregates built up continuously with such bonds, and neglect the complications due to broken bonds on the surface of these aggregates or along some internal defects such as vacancies or dislocations.

Elements of the sp series with 3, 5 or 6 valence electrons per atom can also show covalent structures which can often be approximated by a description using $\pi$ and $\sigma$ bonds, sometimes with some systematically empty or full broken $\sigma$ bonds on each atom (incomplete octets).

The nature of $\sigma$ and $\pi$ bonds in small molecules is most simply analysed in a molecular orbital approximation where each electron is assumed to move through the molecule with a wave function built as a linear combination of atomic orbitals [1], [2], [3]. In its elementary form, each extended electronic function $|\psi\rangle$ can be expressed in terms of the atomic $|s\rangle$ and $|p\rangle$ valence orbitals or in terms of the $|sp^n\rangle = |aJ\rangle$ atomic hybrids which point along the various $\sigma$ bonds $J$ from a site $a$; and of the $|p_\perp\rangle = |a\rangle$ atomic $p$ orbitals which point perpendicular to the $\sigma$ bonds of the site $i$ considered. Here $n = 3, 2$ or 1 depending on the type of $\sigma$ bonds (corresponding respectively to figures 1 a, b or c).

The main characteristics of the bonding are retained if one

- neglects the overlap of orbitals on different sites,
- neglects all matrix elements of the effective one electron Hamiltonian $H$ except (Fig. 3)

$$\langle ap | H | ap \rangle = E_p,$$  \hspace{1cm} (1)
$$\langle aJ | H | aJ \rangle = \frac{E_s + nE_p}{1 + n} = E_0$$  \hspace{1cm} (2)
$$\langle aJ | H | aJ' \rangle = \Delta = \frac{1}{1 + n} (E_s - E_p) < 0,$$  \hspace{1cm} for $J' \neq J$  \hspace{1cm} (3)
$$\langle aJ | H | bJ \rangle = \beta_\sigma < 0,$$  \hspace{1cm} for $b$ near to $a$  \hspace{1cm} (4)
$$\langle a | H | b \rangle = \beta_\pi < 0,$$  \hspace{1cm} for $b$ near to $a$.  \hspace{1cm} (5)

Here $E_s$ and $E_p$ are the energies of the atomic $s$ and $p$ states. $b$ is a site near $a$ along bond $J$.

As there are no cross terms between the $\sigma$ and $\pi$ bonding parts of $|\psi\rangle$, one can consider two independent sets of tight-binding expansions:

$$|\psi_\pi\rangle \approx \sum_{n,J} A_{nJ} |a, J\rangle$$  \hspace{1cm} (6)

with

$$H_\pi \approx \beta_\pi \sum_{n,J} |aJ\rangle \langle bJ\rangle + D \sum_{a,J} |aJ\rangle \langle aJ'\rangle + E_0 \sum_{a,J} |aJ\rangle \langle aJ|$$  \hspace{1cm} (7)

and

$$|\psi_\pi\rangle \approx \sum_{a,J} A_{aJ} |a\rangle$$  \hspace{1cm} (8)

$$H_\sigma \approx \beta_\pi \sum_{a,J} |a\rangle \langle b| + E_\pi \sum_{a} |a\rangle \langle a|.$$  \hspace{1cm} (9)

This is the Hückel approximation [4] for hybrid bonds in its simplest form [6]. The approximations involved in neglecting more indirect transfer integrals are discussed in appendix A. The Hückel model can be directly applied to the macroscopic aggregates considered here. It is clear that, in the absence of broken bonds,
atoms with 3 $\sigma$ bonds ($n = 2$, Fig. 1b) lead to planar hexagonal graphite like networks, or similar networks with some disclinations leading to a finite concentration of five and seven fold rings (Fig. 4c, d);

— atoms with 2 $\sigma$ bonds ($n = 1$, Fig. 1c) lead to linear chains (Fig. 4e).

Systematic breaking of one (sp$^3$) $\sigma$ bond on each atom would lead to corrugated layers (Fig. 5a).

Systematic breaking of two (sp$^3$) $\sigma$ bonds or of one (sp$^3$) $\sigma$ bond on each atom would lead to zigzagging chains or helices (Fig. 5b).

![Fig. 5. Arrays of $\sigma$ (and $\pi$) bonds with systematically broken bonds: a) corrugated layer; b) zigzagging chain.](image)

Because we neglect all but the largest $\sigma$ and $\pi$ transfer integrals, we can hope only for a rough description of the bonds. This seems indeed in better agreement with more elaborate computations for the low energy bonding states than for the more excited antibonding ones [6]. Thus this simple model is in principle especially suited for describing integral properties of the bonds, such as cohesive energy. Its approximate nature is clear from the fact that it neglects the interlayer or interchain interactions, which are certainly weaker than the bond energies, but not completely negligible.

The purpose of this paper is to recall and systematize the cohesive properties of such covalent macroscopic aggregates, when this simple Hückel approximation is used together with a Wigner-Seitz assumption on correlation between valence electrons. We shall compare the results thus obtained to those for pure p bonding or for metallic (sp) bonding.

In a later paper, we shall examine the validity of this Wigner-Seitz assumption, and thus introduce corrections due to interactions between valence electrons.

The continuous transitions actually observed between the various types of bonding discussed here are outside the scope of these two papers, but could be studied from the same point of view.

2. Cohesion of $\sigma$ and $\pi$ bonds in a simple Hückel approximation, when correlations are treated à la Wigner-Seitz. — In their first treatment of cohesion in metals, Wigner and Seitz [7] assumed that the correlation hole around each valence electron has an atomic size, so that each valence electron experiences, in the atom where it moves, a potential which is that of a singly ionized ion, as it would in a neutral gaseous atom. This has indeed been a frequent assumption in band structure computations. With such an assumption, the potential interaction of the electron with the other (neutral) atoms can be neglected; and a summation over the one electron energies in the occupied part of the valence band does not count twice the interaction between electrons, a usual difficulty in one-electron pictures [8].

Thus in this simple approximation, the cohesive energy reads, when referred to monoatomic gases,

$$E_c = - \int_{E_M}^{E_F} n(E) (E - E_a) \, dE$$

(10)

where $E_a$ is the average energy of the valence electrons in isolated atoms, $E_M$ is the Fermi level in the aggregate, and $n(E)$ is the density of states of the valence band per unit energy and per spin. We will count both $n$ and $E_a$ per atom.

If there are $z$ valence electrons per atom,

$$z = \int_{E_M}^{E_F} n(E) \, dE$$

(11)

and, with four sp orbitals per atom

$$0 \leq z \leq Z = 8.$$ (12)

Furthermore $E_a$ is such that

$$\int_{E_M}^{E_F} n(E) E_a \, dE = zE_a = zE_a = 2E_a + (z - 2)E_p \quad \text{for} \quad 2 \leq z \leq 8.$$ (13)

Thus [9]

$$E_c = zE_a - \int_{E_M}^{E_F} n(E) E \, dE$$

(14)

$$\frac{dE_c}{dz} = E_a - E_M \quad \text{for} \quad 0 \leq z \leq 2$$

$$= E_p - E_M \quad \text{for} \quad 2 \leq z \leq 8$$

(15)

In (14) and (15), the slow change of $n(E)$ with $z$ has been neglected, an approximation made through all this paper.

The saturation of the s shell for $z = 2$ in the monoatomic gas of reference introduces a dent in $E_c(z)$, with a slope $dE_c/dz$ increasing discontinuously by

$$E_p - E_a = \delta = (n + 1) | \Delta |.$$ (16)
Except at this point, $E_c(z)$ has everywhere a negative curvature. Finally, it is self evident that

$$E_c(0) = 0 .$$

But we can also write \[ E_c(Z) = \int_{-\infty}^{\infty} n(E) [E - E_c(z)] dE = M_1 = \text{Trace } H = 0 \quad (17) \]
as easily deduced from $E_c(Z) = E_c + 3 E_p$ and from the diagonal parts of $H_e$ and $H_\pi$, equations (7) and (9).

Thus $E_e(z)$ is a continuous function of $z$, starting from zero at both extremities $z = 0$ and $Z = 8$, with two lobes of negative curvature for $0 < z < 2$ and $2 < z < 8$, separated by a dent. It can therefore have one or two maxima. The slope $\delta E_c/\delta z$ at the extremities $z = 0$ and $8$ are related to the band edges, measured respectively from $E_c$ and $E_\pi$. $E_c(z)$ has finite negative discontinuities of the slope

$$\delta E_c/\delta z = - g \quad (18)$$

for each value of $z$ which corresponds to a forbidden gap of width $g$ in the energy band.

To be more specific, we need to study in more details the contributions of $\sigma$ and $\pi$ bonds to the density of states $n(E)$.

2.1 $\sigma$ BONDS. — With the simple Hückel model used here [6], [10], [11], the band structure of the $\sigma$ bonds varies with the bond length $d$, i.e. the ratio between $\beta_\sigma$ and $A$, in the way schematized figure 6a and b.

![Fig. 6. — Band structure of $\sigma$ bonds versus bond length $d$: a) non alternant structures; b) alternant structures. Hatched regions: allowed bands.](image)

— There are furthermore two flat $\pi$ bands (B and AB), with a degeneracy $n - 1/2$ such that, for

$$d < d_c, \quad \text{i.e. } \sum | \beta_\pi | > 1 + n \quad \text{and } A = \frac{1}{2} (E_\pi - E_c) ,$$

the two valence bands contain $1 + n$ valence electrons per atom corresponding to the filling of $(1 + n)\sigma$ bonds per atom.

The symmetry and band edges of the broad $\sigma$ bands can be related to the fact that, in these bands, the energy $E$ of each state can be written (with $E_0$ defined by (2))

$$E = \frac{n - 1}{2} A \pm \sqrt{\beta_\pi^2 + (n + 1)^2 A^2 - \varepsilon + E_0} \quad (20)$$

where $\varepsilon$ is an eigenvalue of the Hamiltonian

$$\mathcal{H} = B \sum \langle a | b \rangle \langle b | a \rangle \quad (21)$$

which describes a narrow $\sigma$ band with a (negative) transfer integral

$$B = - \beta_\sigma A \quad (22)$$
on the same atomic lattice represented figure 3.

The band edges for $E$ can be deduced from the well known result

$$pB \leq \varepsilon \leq - pB . \quad (23)$$

The lower limit of $\varepsilon$ is exactly $- pB$ for alternant structures, such as those of figures 4a, c, e and 5, where only closed circuits of even number of bonds occur (Fig. 6a). The upper limit of $\varepsilon$ is below $- pB$ for non alternant structures, such as those of figures 4b, d; and the difference with $- pB$ mainly measures the relative weight of five fold and sevenfold circuits with respect to the normal sixfold ones (Fig. 6b).

For the flat $\pi$ bands, on the other hand,

$$E = \pm \beta_\pi - A . \quad (24)$$

From the general discussion above, the variation of cohesion with the filling of the $\sigma$ bonds can be pictured figures 7, 8 and 9 respectively for $n = 1, 2$ or 3.

Two essentially different regimes occur if $d_c'$ is defined as in figure 6a, b:

— hybrid regime: for $d < d_c'$, there is a single maximum, corresponding to a well defined peak at $z = \frac{1}{2} Z_\sigma$.

In the first half, the slope $dE_c/\delta z$ varies from $| \beta_\pi |$ (for $z = 0$ and $2 < z < n + 1$) to $| \beta_\pi | - \delta$ (for $z = 2 - e$). In the second half, it varies similarly from $| \beta_\pi | + \delta$ (for $z = n + 1 + e$) to $| \beta_\pi |$ (for $n + 3 < z < 2(n + 1)$). Thus in the extreme hybrid regime $d < d_c'$, $E_c(z_c)$ tends towards a nearly linear peak of slope $\pm | \beta_\pi | ;$
non hybrid regime: for \( d > d' \), there are two broad and continuous maxima. From general theorems on energy broadening at level crossings, it is expected that the average energies of the two broad sp bands, figure 6, are respectively below

\[ \beta_{\sigma} + \frac{E_s + E_p}{2} \]

and above

\[ \beta_{\sigma} + \frac{E_s + E_p}{2} \]

but tend towards these limits for large \( d \). We can therefore state that the maxima occur respectively for \( 1 < z_\sigma < 2 \) and \( 1 + n < z_\sigma < 2 + n \), and tend towards 1 and \( 2 + n \) in the limit of large \( d \). In that limit, the secondary minimum at \( z_\sigma = 2 \) tends obviously faster towards zero than \( E_c(z_\sigma) \) itself.

The two regimes are limited by a critical distance \( d' \), which is somewhat smaller than the crossing distance \( d_e \) (Fig. 6). Thus

\[
\text{while for } d \geq d', \quad |\beta_{\sigma}| \leq \delta = E_p - E_s
\]

or

\[
\text{or } d \geq d_e, \quad 2 |\beta_{\sigma}| \leq \delta.
\]

For \( d \) increasing through \( d_e \), the discontinuity of slope present at \( z_\sigma = 1 + n \) disappears. But this detail does not change the overall picture.

When the \( \sigma \) bonds are just full, i.e.

\[ z_\sigma = \frac{1}{2} Z_\sigma = 1 + n, \]

one obtains what can be called the \( \sigma \) bonding energy. It is the maximum cohesion in the hybrid regime, but below it in the non hybrid one. This is

\[
E_c(1 + n) = (1 - n)(\beta_{\sigma} - \Delta) - \int_{E_1}^{E_3} n_{sp}(E)(E - E_0)\,dE + (1 + n)\Delta. \tag{25}
\]

The first term is the contribution from the flat bonding p band. \( n_{sp}(E) \) is the density of electronic states, per unit energy and atom, in the broad valence sp band, with limits \( E_1 \) and \( E_3 \), figure 6. The last term is the negative term due to the sp promotion of the \( (1 + n) \) electrons involved from configuration \( s^2 p^{n-1} \) to configuration \( sp^n \).

Using the symmetry properties of the sp bands and a moment development, one can show (Appendix B)
that, in the hybrid regime, the σ bonding energy can be written as

\[ E_\sigma(1 + n) = (n - 1) | \beta_\sigma | + 2 \pi | \beta_\sigma | - (1 + n) | \Delta | \]  

(26)

where \( \alpha \) can be taken as unity to better than 10%.

Here

\[ \beta_\sigma = -\sqrt{\beta_\sigma^2 + \frac{(1 + n)^2 \Delta^2}{4}}. \]  

(27)

Thus equation (26), with \( \alpha = 1 \), is a good approximation in a model which is anyway very rough. It is valid up to larger values of \( d \) than the development in \( \Delta/\beta_\sigma \) obtained previously [11]. We shall use it in the following discussion.

If we introduce the band gap (Fig. 6)

\[ g = 2 | \beta_\sigma | - (1 + n) | \Delta | \]  

(28)

we obtain the relationship

\[ E_\sigma(1 + n) \approx \left( \frac{n - 1}{2} \right) \left[ g + (1 + n) | \Delta | \right] \]

\[ + \sqrt{\left( g + (1 + n) | \Delta | \right)^2 + (1 + n)^2 \Delta^2} - (1 + n) | \Delta |. \]  

(29)

In the extreme hybrid limit \( d \ll d_\text{c} \), these equations reduce to [11]

\[ E_\sigma(1 + n) \simeq (1 + n) (| \beta_\sigma | - | \Delta |) \simeq \frac{1 + n}{2} \left( g + (n - 1) | \Delta | \right). \]  

(30)

Figure 10 pictures \( E_\sigma(\varepsilon) \) in this limit.

In the non hybrid regime, one could give a similar development in \( | \beta_\sigma | / | \Delta | \). In the extreme non hybrid regime \( d \gg d_\text{c} \), it is clear that the s and p bands become independant. Figure 11 pictures that limit for \( n = 1, 2, 3 \), using the fact that the non degenerate atomic level which broadens into a band of width \( w = 2 | \beta_\sigma | \) contributes to cohesion a nearly parabolic term of maximum value \( \frac{w}{4} \simeq \frac{1}{2} | \beta_\sigma | \).

2.2 π BANDS — π bands arise in unsaturated structures with σ bonds, where \( n = 1 \) or 2.

For \( n = 1 \), the chains structures (Fig. 4e) have two orthogonal (resonant) π bands, corresponding to \( p_x \) and \( p_y \) orbitals respectively. Thus the density of states in the π bands is (Fig. 12a)

\[ n_\pi(E) = \frac{4}{\pi \sqrt{4 \beta_\pi^2 - (E - E_\pi)^2}}. \]  

(31)
and the contribution to cohesion is, per atom

\[ E_n(z_n) = -\int_{E_p + 2\beta_n}^{E_p} n_n(E) (E - E_p) \, dE \]

\[ = \frac{4}{\pi} \sqrt{4\beta_n^2 - (E_p - E_n)^2} \]

with

\[ z_n = \int_{E_p + 2\beta_n}^{E_p} n_n(E) \, dE \]

\[ = \frac{4}{\pi} \text{Arcos} \left( \frac{E_p - E_n}{2\beta_n} \right) \]  

Thus (Fig. 12b)

\[ E_n(z_n) = \frac{2w_n}{\pi} \sin \left( \frac{\pi}{4} z_n \right) \]  

(32)

with

\[ w_n = 4 \mid \beta_n \mid . \]  

(33)

For \( n = 2 \), the plane structures pictured figures 4c, d with one resonant p orbital per atom, lead to a density of states \( n_n(E) \) with a finite value at the lower edge of the \( \pi \) band (\( E = E_p + 3\beta_n \)). \( n_n(E) \) is further symmetrical with respect to \( E_p \) for alternate structures (Fig. 4c), but has an upper edge below \( E_p - 3\beta_n \) for non alternate structures (Fig. 4d). An analysis similar to those for s and d bands in metals [8], [9] shows that, for the structures involved, the cohesive energy is given, to a good approximation, by a rough assumption about \( n_n(E) \), for instance a rectangular band, symmetrical with respect to \( E_p \) :

\[ n_n(E) \simeq \frac{2}{w_n} \]  

for \( E_p + 3\beta_n \leq E \leq E_p - 3\beta_n \)  

with

\[ w_n = 6 \mid \beta_n \mid . \]  

(34)

Hence

\[ E_n'(z_n) \simeq -\int_{E_p + 3\beta_n}^{E_p} \frac{2}{w_n} (E - E_p) \, dE \]

with

\[ z_n \simeq \int_{E_p + 3\beta_n}^{E_p} \frac{2}{w_n} \, dE \]

or

\[ E_n'(z_n) \simeq \frac{z_n}{2} \left( 1 - \frac{z_n}{2} \right) w_n'. \]  

(36)

With the definitions (33), (35) of the widths, it is seen that this parabolic variation of cohesion with the filling of the band is not very different from the sinusoidal variation (32) for \( n = 1 \), if cohesion is counted per bonding \( \pi \) electron: the maximum bonding is \( E_n'(1) = \frac{3}{2} \mid \beta_n \mid = 1.5 \mid \beta_n \mid \) for \( n = 2 \), compared with \( E_n'(2) = \frac{8}{\pi} \mid \beta_n \mid \simeq 2.6 \mid \beta_n \mid \) for \( n = 1 \) (cf. Fig. 13).

2.3 ELEMENTARY STRUCTURES WITH INCOMPLETE OCTETS, i.e. BROKEN \( \sigma \) BONDS. — As pointed out in figure 5, some elementary structures can be thought of as built with \( \sigma \) and \( \pi \) (resonating) bonds, but with some \( \sigma \) bonds systematically broken on each atom [1]. These broken bonds are expected to lead to electronic states in the \( \sigma \) band gap. In most observed elementary structures, these states are completely full or completely empty.

The band structure of such cases can be analysed by a direct and straightforward extension of that used for normal (complete) \( \sigma \) bonding [6], [10], [11]. This is detailed in appendix C. Figures 14, 15, 16 give the band structure versus the interatomic distance \( d \) for various cases of interest:

- for sp\(^3\) : corrugated layers with \( p = 3 \) neighbours and \( q = 1 \) broken \( \sigma \) bond (Figs 5a and 14).
- zigzag saturated chains with \( p = 2 \) neighbours and \( q = 2 \) broken \( \sigma \) bonds (Figs. 5b and 15).
- for sp\(^2\) : zigzag conjugated chains with \( p = 2 \) neighbours and \( q = 1 \) broken \( \sigma \) bond (Fig. 16).
FIG. 13. — Schematic : a) density of states assumed for \( \pi \) simple resonating bonds in planar arrays; b) corresponding cohesive energy.

FIG. 14. — Structure with one \( sp' \) broken bond per atom (hatched regions allowed). Two pure \( p \) flat bands (B, AB) with one state per atom each.

FIG. 15. — Structure with two \( sp' \) broken bonds per atom (hatched regions allowed). One \( sp' \) flat band with two states per atom.

FIG. 16. — Structure of \( \sigma \) bonds for one \( sp' \) broken bond per atom (hatched regions allowed). No flat \( p \) band.

The figures are drawn for *alternant structures* [11]. Non alternant structures would have allowed bands inside the hatched regions, with some of the boundaries slightly different from the maximum extension pictured figures 14 to 16.

If there is one broken \( \sigma \) bond per atom, it introduces, in the hybrid limit \( d < d_c' \), an intermediate band centered on the average energy \( E_0 = \frac{E_s + nE_p}{1 + n} \), and reduces correlative the degeneracy of the pure \( p \) (B and AB) flat bands. The broken bond energy \( E_0 \) is broadened into a band by the fact that electrons are delocalized and, owing to \( A = \langle aJ | H | aJ' \rangle \neq 0 \) (eq. 3), can jump from one broken bond to another by making an intermediate transition through unbroken bonds.

In the strong hybrid limit \( d \ll d_c' \), thus \( | \beta_\sigma | \ll \delta \), this intermediate band has limits \( E_0 \pm \frac{qP}{\beta_\sigma} A^2 \). It is therefore narrow. The decrease in degeneracy or suppression of the two \( p \) (B and AB) flat bands is compensated by an increase in the lower limits of the broad \( sp \) bands. It can be shown (Appendix C) that, to terms of order \( A^2/\beta_\sigma \), the average energies of the broad \( sp \) bands are at the middle of each band, thus at energies \( E_0 \pm \beta_\sigma \) for figure 16 and

\[
E_0 \pm \beta_\sigma + \frac{A}{2}
\]
for figure 14. The neglected terms in $\Delta^2/\beta_\sigma$ broaden the total band system, thus shift the lower sp band towards lower energies and the upper sp band towards higher energies.

Finally, as one approaches the hybrid limit $d = d_\alpha'$, the intermediate band mixes with the valence band. In that limit, it has acquired a width of the order of several $|\Delta|$, thus comparable to that of the valence band. The whole band structure is then nearly continuous, with a total width somewhat smaller than $2(E_p - E_s)$.

With two broken bonds per atom (Fig. 15), the two (B and AB) flat p bands are replaced by one flat band of constant energy $E_p$, corresponding to p states strictly localized on the broken bonds. The other (sp) states originating from the broken bonds give rise to a band which is centered at $E_n + E_p^2/2$.

The width of this band is again $2pq\Delta^2/|\beta_\sigma|$. The bonding and antibonding broad sp bands are again shifted towards higher energies, their width being reduced by one third in the strong hybrid limit. In that limit, each of these bands has an average energy $E_0 \pm \beta_\sigma$ to corrections of order $\Delta^2/\beta_\sigma$ which would again shift the two bands further apart.

It is easily checked that, in the strong hybrid limit, the total electronic density of the intermediate bands due to broken bonds tends towards that of the sp$^3$ orbitals localized on those bonds. This result is self evident: when one neglects $\Delta$ with respect to $\beta_\sigma$, the electrons are localized on their sp$^3$ bonds.

This summary description allows a simple description of how the cohesive energy $E_c(z_\sigma)$ due to these sp$^3$ bonds varies with the number $z_\sigma$ of sp$^3$ electrons per atom. This is pictured in figures 17, 18 and 19. Results in the extreme hybrid limit, when terms in $\Delta^2/\beta_\sigma$ are neglected, are shown by continuous lines. Corrections due to terms in $\Delta^2/\beta_\sigma$ would increase somewhat $E_c$ without changing the general picture, assuming they remain small, thus $d \ll d_c$.

3. Discussion of cohesion. — A full discussion of cohesion within the simple Hückel model developed here would require, for each structure, an exact computation of the density of states $n(\sigma)$. This has not yet been done systematically, and would no doubt be of some interest.

Experimentally, figure 20 shows that, when computed with the monoatomic gas as a reference [1], the cohesive energy of each sp series shows a marked peak for the tetravalent elements, where the total number $z$ of s and p valence electrons per atom equals 4.

The hybrid sp$^n$ covalent structures such as those analysed above are prominent in the middle of the light series, with metals on the left and covalent p molecules on the right. They disappear in the heavy series.

A qualitative discussion of these features involves a knowledge of the relative values of the two parameters $\beta_\sigma$ and $\delta = E_p - E_s$ which dominate the hybrid $n$ structures. Roughly speaking, $|\beta_\sigma|/\delta$ decreases from the top left to the bottom right of the periodic table, in such a way that, for the tetravalent elements in the sp$^3$ diamond cubic structure, $d/d_c$ increases when going down the periodic table, but remains less than unity except for grey tin [6], [11] (Fig. 6).
FIG. 20. — Cohesive energies (in eV per atom) for the elements of the sp series, counted from the monoatomic gas [1], [20]. $M_{sp}$ : metallic sp bonding; $C_{sp}$ : covalent hybrid sp bonding; $p$ : $p$ bonding (the boundaries are approximate). The notation for each series is given on the left of the list of elements.

3.1 $z = 4$. — The marked peak in cohesion observed for $z = 4$ can qualitatively be related to the special stability of the diamond structure, with its especially large gap (Fig. 7). The decrease when going down the periodic table is related to the decrease in $d/d_c$ and corresponding decrease in energy gap.

An order of magnitude of the transfer integral $\beta_a$ can be deduced from the observed promotion energy $\delta = 4 | \Delta |$ and from the energy gap $g$ between valence and conduction bands. Table I gives the experimental values of $\delta$ and $g$, where for $g$ the minimum values related to the indirect gap are used [12], [13]. The values of $\delta$ are somewhat uncertain, because the terms related to sp$^3$ configurations are poorly known, and because some simplifying assumptions must be made to deduce $\delta$ [14], [15], [16], [17]. This point will be further studied in a next paper. The values of $\beta_a$ thus deduced from equation (28) are of the same order of magnitude as those deduced by Harrison [18] from band structure computations (cf. Appendix A).

No exact fit can be expected, because, as pointed out before, the tight-binding approximation used here is only approximate for the valence band, and very poor for the conduction band.

From the values of $\beta_a$ deduced from equation (28), and also given in Table I, one deduces that

$$\frac{1}{2} \delta < | \beta_a | < \delta .$$

Thus, as stated above, the three elements, C, Si, Ge are on the left of the crossing point $d_c$, figure 6, but they are not strictly in the hybrid case:

$$d_c < d < d_c .$$

The use of equation (29) should nevertheless give a reasonable approximation of a more exact computation of $E_c$.

Table I shows that the values of the cohesive energy for the diamond structure

$$E_c(4) = 2 | \beta_a | - \delta + \frac{\sqrt{4 \beta_a^2 + \delta^2}}{2}$$

deduced from the observed values of $\delta$ and $g$ are decreasing from C to Si, in agreement with the measured values of cohesion (1).

We find that, for tetravalent elements, the cubic and hexagonal arrangements of tetrahedral sp$^3$ bonds should have the same cohesive energy, while in fact the cubic structure is more stable. However measurements of the splitting of dislocations [19] show that the energy difference between the two phases, although finite, is small in Si and Ge. It is related to transfer integrals between sp$^3$ orbitals which do not point along a common bond, and are thus small and neglected here [20].

We find also that, for tetravalent elements, these two structures (diamond cubic and diamond hexagonal) should be more stable, at low temperatures, than any of the other phases discussed above. The difference in energy is however a minimum for the graphitic layer structure, with an energy

$$E_c(3) + E_c(1) =$$

$$= \frac{1}{2} [ 2 | \beta_a | - \delta + \sqrt{4 \beta_a^2 + \delta^2} ] + 1.5 | \beta_a | .$$

(1) The experimental values of cohesion have been corrected to refer to the monoatomic gas [1], [12]. Numerical errors affect the values of $\delta$ used in reference [11].

| Table I |
| --- | --- | --- | --- | --- |
| Elements | $\delta$ | $g$ | $\frac{1}{2}(\delta + g)$ | $| \beta_a |$ | Harrison | from (29) | Measured |
| C | 8 | 2.5 | 1.15 | 6.75 | 5.25 | 21.2 | 7.4 |
| Si | (6.5) | 7.5 | 3.8 | 3.27 | 2.2 | 11.4 | 4.6 |
| Ge | 7 | 0.75 | 3.9 | 2.05 | 2.0 | 11.2 | 3.9 |
From the fact that \(| \beta_\sigma | < \delta < 2 | \beta_\sigma | \) and \( \beta_\sigma \approx 0.2 \beta_\sigma \), the difference in energy between the diamond cubic and graphitic layer structures is sizeable (about 1.5 \(| \beta_\sigma | \)). But it can be argued that the energy of interaction between layers in the three-dimensional graphitic structure could be strong enough to explain that, for carbon, the graphitic structure is the most stable one at low temperatures.

It is however clear from table 1 that the absolute magnitude of the computed cohesions are much too large. We believe this misfit to stem from the approximations used in the Hückel model as developed here. This will be fully discussed in a subsequent publication. We will show that the corrective terms are not very structure sensitive. As a result, the use of the simple Hückel model might have a meaning when comparing the relative stability of phases, even if the absolute cohesion is poorly analysed.

3.2 \( z < 4 \) — The extreme hybrid approximation should allow a comparison for \( z < 4 \) of the stability of the diamond cubic and hexagonal phases with other possible phases.

— Figures 21, 22 show that, for \( z < 4 \), these two diamond structures should be more stable than any other possible hybrid sp\(^n\) structure. The graphite layers structure has the strongest stability after the diamond one.

It should however be pointed out again that all layers or chains structures have been analysed neglecting their interactions. This is inherent in the simple Hückel model used here, but probably underestimates somewhat the stability of these layers and chains structures, where these interactions are known to modify markedly the band structures.

— All sp\(^n\) hybrids start at \( z = 0 \) with a slope \( \frac{dE_c}{dz} \) equal to \( | \beta_\sigma | \). For small \( z \), they are thus necessarily less stable than phases which have smaller transfer integrals, but many more neighbours, so that their sp band has a larger width and a lower energy edge. Such structures, which do not respect the hybrid bond angles, have necessarily a gapless sp band, thus are metallic. The most stable for small values of \( z \) will obviously be the most compact [8], with the larger number of neighbours \( p = 12 \). Figure 23 pictures schematically such a band structure, which is studied here in the hybrid range \( d \ll d_c \).

Such a compact metallic sp structure will have a cohesive energy with the following characteristics

\[
\frac{dE_c}{dz} = 12 | \beta_\sigma | \approx 4 \beta_\sigma \quad \text{for} \quad z = 0
\]

\[
- \frac{dE_c}{dz} = 12 | \tilde{\beta}_p | \approx 4 \beta_\sigma \quad \text{for} \quad z = 8.
\]

\( \tilde{\beta}_p \) is here an angular average of various possible pp transfer integrals, which is much smaller in amplitude than the maximum value \( \beta_\sigma \) introduced in appendix A, and probably smaller in amplitude than \( \beta_\sigma \).

Finally in the intermediate range of \( z \), \( E_c(z) \) can be roughly represented as due to a band of constant
density and width $w$ centred on the energy $E_0$. Taking, from second moments arguments [8], [21],

$$w \approx 3 \sqrt{2 | \beta |},$$

where $\beta$ is an average of $\beta_s$ and $\beta_p$, probably smaller in amplitude than $\beta_s$, this gives in the central part of the series (cf. Appendix A):

$$E_s(z) \leq 4 \sqrt{2 | \beta_p |} \left(1 - \frac{z}{8}\right) - z(E_0 - E_a)$$

where (cf. equation (13))

$$z(E_0 - E_a) = \frac{3}{4} \delta \quad \text{for} \quad 0 < z < 2$$

$$= \left(1 - \frac{z}{8}\right) 2 \delta \quad \text{for} \quad 2 < z < 8.$$  

This variation, pictured in figure 22d, predicts the metallic sp compact structures to be preferred for $z$ small, up to 2 or 3. But the diamond cubic structure should be preferred for $z = 4$.

However even for $z = 4$, the difference in energy is small, so that it is not surprising that liquid Si, Ge and Sn adopt an amorphous structure which is compact and metallic.

3. 3 $z > 4$. — In this range, the extreme hybrid case would still predict the diamond structure to be the most stable of the hybrid sp$^n$ structures (Figs. 21, 22); but it is not valid, even in the first sp series.

Inspection of figures 6 and 14-16 however shows that all sp$^n$ structures have the same upper limit to their band structures, with the largest degeneracy of flat p band in the diamond structure. For all ratios of $d/d_s$, therefore, one expects, in the simple Hückel model developed here, the diamond structures to be the most stable of the sp$^n$ hybrid structures, for large values of $z$ and at least for $z > 6$. This is because for such structures $dE_c/dz$ is linear with the largest negative slope for $z > 6$.

Inspection of figures 6, 14-16 however also shows us that, for $d \approx d_e$ or $d > d_e$, the differences in energy between the various structures should be less marked than for $d \ll d_e$. For $d = d_e$, the structures pictured figures 14 and 15 should have a special stability for respectively $z = 5$ and 6, because of the gaps present in that range (a similar gap present in the $\sigma$ bands of the structure figure 16 is mostly compensated by the presence of a $\pi$ band in that range of energy). If one takes into account the interlayers or interchains interactions [22] neglected here, it is thus not surprising to observe structures near to the corrugated layers of figure 14 for As ($z = 5$) and near to zigzag chains, helices and rings for S, Se and Te in their crystal and amorphous phases.

In the range considered, $d > d_e$, the non hybrid structures to be compared with these sp$^n$ hybrid ones are built up with p orbitals because the s and p bands mix only little. These p covalent structures require however some discussion:

1. — The equivalent to the sp metallic state described for $z < 4$ is the simple cubic p covalent structures, made up of three sets of parallel and intercrossing but independent chains of p bands (Fig. 24a). A discussion analogous to that for $\pi$ bonding shows that the cohesive energy is for ($2 < z < 8$)

$$E_p = \frac{12 | \beta_p |}{\pi} \sin \frac{\pi}{6} (z - 2).$$

![Fig. 24. Different types of p covalent bondings: a) simple cubic; b) corrugated layers; c) zigzag chains; d) diatomic molecules.](image-url)
increasing with \( \delta|/ \beta_s \), i.e. when going down the periodic table. Taking into account the larger stability of the chain compounds observed for \( z = 6 \), it is not surprising to observe the simple cubic structure in the \( z = 5 \) and \( 6 \) columns at normal pressure (2) only for polonium, i.e. at the bottom of the periodic table. In the liquid and amorphous phases, the layers and chains structures are preserved for \( z = 5 \) and \( 6 \), except for Te at very high temperatures where a short range order similar to that of the simple cubic structure is observed [23].

2. — For \( z = 7 \), the expected simple cubic structure is replaced by p bonding in diatomic molecules (Fig. 20d).

This might look surprising as the cohesive energy of the molecules would be (in the Hückel model) equal to \(| / \beta_p \| \), while the simple cubic structure gives \( 2|/ \beta_p \| \). In fact, the arrays of diatomic molecules can probably be thought of as resulting from an extreme dimerization process on the chains. One knows indeed that periodic modulation necessarily occur at low temperatures in metallic chains [24]; and they can be extreme if the inner shells are small, thus especially on the top right of the periodic table. As a result of such dimerization, the interatomic distances are shorter, thus | / \beta_p | is larger, in the molecules than in the cubic phase; but also the intermolecular interactions are not negligible.

When going down the periodic table, the layers and chains observed for \( z = 5 \) and \( 6 \) have bonding angles which decrease [1] from somewhat less than 109° to not much more than 90°. They can be thought of as having an amount of p character larger than that for sp\(^3\). Layers and chains with pure p characters are pictured figure 20b and c. They would have respectively 3 and 2 bonds per atom, and can again be thought of as less extreme dimerization of the simple cubic.

3. — Going back to the known cases of a simple cubic (p covalent) metallic structure, it is clear that the absence of dimerization, or more generally of bond alternation, comes from the presence of very large inner shells which prevent large distortions. One would however expect some small periodic modulations to occur at low temperatures, and thus change the equilibrium lattice structure [25]. This point does not seem to have been studied (3).

4. Conclusion. — The very elementary Hückel model, taken in its simplest form, can only account for a rough description of cohesion of elements in the sp series. It explains the qualitatively strong peak in cohesion observed in the middle of the series, connected with the diamond cubic structure, and its decrease when going down in the periodic table. It explains that compact metallic sp structures are preferred on the left of the series and covalent p structures on the right. Fairly reasonable values of the transfer integral \( \beta_s \) are deduced from the energy gap for tetravalent solids.

The main weaknesses are as follows:

— The absolute magnitudes of cohesion computed are too large.
— The peak in cohesion observed for \( z = 4 \) is sharper than computed.
— The special stability of layer and chain structures observed for \( z = 4, 5, 6 \) very probably involves fairly strong interlayer or interchain interactions which have not been taken into account here.
— The stability of diatomic molecules observed for \( z = 7 \) must involve in a similar way some sizeable intermolecular interactions.

The discussion has mostly been based on approximate expansions for \( d \leq d_c \) or \( d > d_c \). It would be of interest to compute exactly the relative stability of phases in this model for all distances \( d \).

Further work should include a study of the possible continuous transitions between the extreme cases considered here: bonding angles varying continuously from 109° to 90° in layer and chain compounds; continuous variation of nearest and next nearest neighbours interactions in dimerization.

Finally a more thorough study would also take into account the short range repulsive terms which account for the equilibrium atomic volumes and for the bulk modulus [26]. These terms would lead to possible variations of atomic volumes and thus of transfer integrals with the different phases discussed.

Appendix A. — Remar Ks on the sp\(^n\) Transfer Integrals. — The sp\(^n\) transfer integrals can be expressed in terms of

\[
\beta_s = \langle s^a | V_s | s^a \rangle \\
\beta_p = -\langle p^a_s | V_s | p^a_s \rangle \\
\beta_{ps} = \langle p^a_s | V_s | p^b \rangle
\]

where \( a \) and \( b \) are two atoms along the \( z \) axis and \( \beta_s, \beta_p \) and \( \beta_{ps} \) are negative.

Thus the transfer integral along a \( \sigma \) bond can be written as follows:

— for sp:

\[
\beta_s = \frac{1}{2} \langle s^a + p^a_s | V_s | s^b - p^b_s \rangle = \frac{1}{2}(\beta_s + \beta_p + 2 \beta_{ps})
\]

References:
1. Phosphorus and antimony present the same phase under pressure [27].
2. The other metallic solids discussed here are semimetals, with small densities of states at the Fermi level. In graphic layers, this occurs by a special folding of the \( E(k) \) curves which leads to a vanishing density of states for a half filled band (cf. Appendix D). In such two or three dimensional semimetals, the electron-phonon terms responsible for the lattice modulations are small [25].
In a similar way, the transfer integrals between two \( sp^n \) hybrids which do not point along the same bond are as follows (Fig. A.1):

![Diagram](image)

**Fig. A.1. — Notations for saturated and broken \( s \) bonds.**

The neglect of these transfer integrals with respect to the direct ones (A.2) to (A.4) involves some assumptions about the relative values of \( \beta_s, \beta_p, \) and \( \beta_{ps} \).

Because of the signs of these three integrals, and if they are of comparable amplitudes, it is seen that (A.5) to (A.7) are indeed small compared with (A.2) to (A.4).

This is also true for even more indirect transfer integrals, such as \( \langle aJ' | V_s | bJ'' \rangle \) or \( \langle aJ' | V_s | bJ'' \rangle \), figure A.1. For instance one easily finds

\[
\langle aJ' | V_s | bJ'' \rangle = \frac{1}{4} \langle s^a + p_s^a - p_s^b - p_s^b | V_s | s^b - p_s^b - p_s^b \rangle = \frac{1}{4} (\beta_s - \beta_p) + \frac{\sqrt{3}}{6} \beta_{ps}.
\]

A numerical estimate can be made if one assumes, following Pauling [1], the following values of the integrals:

\[
\begin{align*}
\beta_p & = 1.732 \beta_s \quad \text{(A.10)} \\
\beta_s & = 2 \beta_s \quad \text{for } sp^3 \quad \text{(A.11)}
\end{align*}
\]

so that

\[
\beta_{ps} = 0.578 \beta_s. \quad \text{(A.12)}
\]

This gives the values of table A.1 for the various transfer integrals.

<table>
<thead>
<tr>
<th>Table A.1</th>
<th>Values of transfer integrals in terms of ( \beta_s ) (according to Pauling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta_s )</td>
<td>sp</td>
</tr>
<tr>
<td>( \langle aJ'</td>
<td>V_s</td>
</tr>
<tr>
<td>( \langle aJ'</td>
<td>V_s</td>
</tr>
</tbody>
</table>
Similar results obtain from the values deduced by Harrison [18] from band structure computations:

\[ \beta_p = \frac{3.24}{1.40} \beta_s = 2.31 \beta_s \quad (A.13) \]
\[ \beta_{ps} = \frac{1.84}{1.40} \beta_s = 1.31 \beta_s \quad (A.14) \]
\[ \beta_n = \frac{0.81}{1.40} \beta_s = 0.58 \beta_s \quad (A.15) \]

with

\[ \beta_s = 1.40 \frac{\hbar^2}{md^2} \quad (A.16) \]

where \( d \) is the interatomic distance. The corresponding values of transfer integrals are given in Table A. II.

### Table A. II

| Values of transfer integrals in terms of \( \beta_s \) (according to Harrison) |
|-----------------|------------------|------------------|------------------|
|                | \( \beta_s \)    | \( \beta_{sp} \) | \( \beta_{sp^2} \) |
| \( \langle aJ \mid V_{as} \mid bJ \rangle \) | 2.97             | 3.11             | 3.12             |
| \( \langle aJ' \mid V_{as} \mid bJ \rangle \) | -0.65            | -0.13            | 0.05             |

With either of these sets of values, the approximation is especially good for \( sp^3 \). It is also seen that, for the same interatomic distances, the direct transfer integrals are similar for the various hybridization \( sp^n \) \((n = 1, 2, 3)\).

In the text, we use finally a simplified version of Harrison’s results:

\[ \beta_p \simeq 4.20 \frac{\hbar^2}{md^2} \quad (A.17) \]
\[ \beta_{ps} = 2.3 \beta_s \quad (A.18) \]
\[ \beta_n = 0.2 \beta_s \quad (A.19) \]

### Appendix B — Approximate Formula for the Cohesion of \( \sigma \) Bonding

Using equations (20) and (24), equation (25) can be written

\[ E_s(1 + n) = (1 - n) \beta_s + 2 n \Delta + \int_{\varepsilon_1}^{\varepsilon_2} n(e) \left( \frac{1 - n}{2} \Delta + \sqrt{\beta_s^2 + \frac{(1 + n)^2}{4} \Delta^2 - \varepsilon} \right) d\varepsilon \quad (B.1) \]

where \( n(e) \) is the density of states per unit energy \( \varepsilon \) and per site for the \( s \) band problem (21), (22). \( \varepsilon_1 \) and \( \varepsilon_2 \) are the energies \( \varepsilon \) related to \( E_1 \) and \( E_2 \) by equation (20). Finally, with

\[ n(e) = \int_{\varepsilon_1}^{\varepsilon_2} n(e) d\varepsilon = 2 \quad (B.2) \]

one obtains

\[ E_s(1 + n) = (1 - n) \beta_s + (1 + n) \Delta + \int_{-(1 + n)\beta_s}^{-(1 + n)\beta_s} \times \left( \sqrt{\beta_s^2 + \frac{(1 + n)^2}{4} \Delta^2 - \varepsilon} \right) d\varepsilon \quad (B.3) \]

In the hybrid limit \( d \leq d_c \), an expansion of the square root in powers of \( \varepsilon \) gives

\[ E_s(1 + n) = (1 - n) \beta_s + (1 + n) \Delta - \beta_s^* \times \left( \frac{\mathcal{M}_0}{p} + \frac{\mathcal{M}_1}{p^2} - \frac{1}{8} \frac{\mathcal{M}_2}{\beta_s^*} + \cdots + \frac{1}{p} \frac{1}{(1 - p) + 1} \frac{\mathcal{M}_p}{\beta_s^*} + \cdots \right) \quad (B.4) \]

where

\[ \beta_s^* = -\sqrt{\beta_s^2 + \frac{(1 + n)^2}{4} \Delta^2} \quad (B.5) \]

and

\[ \mathcal{M}_p = \int_{\varepsilon_1}^{\varepsilon_2} \nu(e) e^p d\varepsilon \quad (B.6) \]

For the covalent structures pictured [10] figures 4 and 5,

\[ \mathcal{M}_0 = 2 \quad (B.7) \]
\[ \mathcal{M}_1 = 0 \]
\[ \mathcal{M}_2 = 2(1 + n) \beta_s^* \Delta^2 \]
\[ \mathcal{M}_3 = 0 \]
\[ \mathcal{M}_4 = 2(1 + n)(1 + 2 n) \beta_s^* \Delta^4 \]

For periodic structures (infinite linear chains, hexagonal planes, cubic or hexagonal in space).

\[ \mathcal{M}_{2p+1} = 0 \quad (B.8) \]
\[ \mathcal{M}_6 = 2 \{ (1 + n)(1 + 4 n + 5 n^2) + m_6 \} \beta_s^* \Delta^6 \quad (B.9) \]

where

\[ m_6 = 36 \text{ for } n = 3 \]
\[ = 6 \text{ for } n = 2 \]
\[ = 0 \text{ for } n = 1 \]

For two or three dimensional amorphous structures, \( \mathcal{M}_5/\beta_s^* \Delta^5 \) and \( \mathcal{M}_7/\beta_s^* \Delta^7 \) are of order unity, and
$\mathcal{K}_6/\beta_6 \Delta^k$ is correlatively reduced by an amount smaller than $m_6$.

It is then easy to check that the following approximation holds for $d \leq d_c$:

$$E_d(1 + n) = (n - 1) |\beta_\sigma| + 2 \alpha |\beta'_\sigma| - (1 + n) |\Delta|.$$  \hfill (B.10)

$\beta'_\sigma$ is given by (B.5) and the numerical factor

$$\alpha = 1 - \frac{1}{2(1 + n)} \frac{u}{(1 + u)^2} - \frac{5}{8} \frac{1 + 2n}{(1 + n)^3} \frac{u^2}{(1 + u)^4} + \cdots$$ \hfill (B.11)

can be taken as unity to better than 10% in the covalent range $d \leq d_c$, where

$$u = (1 + n)^3 \Delta^2/4 \beta^2_\sigma \leq 1.$$ \hfill (B.12)

In that range, inspection of the first terms of series (B.11) indicates that it probably converges rapidly, especially for large values of $n$; the corresponding value of $\alpha$ depends very little on the actual structure considered, whether amorphous or crystalline.

**Appendix C** — **Extension of Leman’s [6] and Thorpe and Weaire’s [10] Theorem to Elementary Structures with Broken \sigma Bonds.** — We assume an elementary structure where every atom has $p\sigma$ (sp*) bonds $J$ and $q$ supplementary broken (dangling) bonds $L$ (Fig. A.1).

An extension of assumptions (1) to (4) of the text is to assume further

$$\langle aJ \mid H \mid aL \rangle = \langle aL \mid H \mid aL' \rangle = \Delta$$

(for $L' \neq L$). \hfill (C.1)

We follow the same line of argument as in references [10].

A development of $|\psi\rangle$ as in references [10].

A development of $|\psi\rangle$ as

$$|\psi\rangle = \sum_{a,\sigma=L,J} A_{ax} |a_x\rangle$$ \hfill (C.2)

with

$$H|\psi\rangle = E|\psi\rangle$$ \hfill (C.3)

leads to the set of linear equations in the coefficients $A_{ax}$:

$$(E + \Delta) A_{aj} = \Delta \rho_a + \beta_a A_{bj}$$ \hfill (C.4)

$$(E + \Delta) A_{aj} = \Delta \rho_a + \beta_a A_{aj}$$ \hfill (C.5)

$$(E + \Delta) A_{al} = \Delta \rho_a$$ \hfill (C.6)

where

$$\rho_a = \sum_j A_{aj} + \sum_l A_{al}.$$ \hfill (C.7)

and

$$E_0 = \frac{E + nE_2}{1 + n} = 0.$$ \hfill (C.8)

C.1 **Broad sp bands.** — Let us first assume

$$E + \Delta \neq 0 \text{ and } \rho_a \neq 0.$$ \hfill (C.9)

Equation (C.6) gives

$$A_{al} \frac{\Delta}{E + \Delta} \rho_a$$

and equations (C.4) and (C.5) give in turn, by eliminating $A_{bj}$,

$$(E + \Delta) A_{aj} = \Delta \rho_a + \frac{\beta_a}{E + \Delta} (\Delta \rho_b + \beta_a A_{aj}).$$ \hfill (C.10)

If there are $q$ broken bonds per atom, (C.7) gives

$$\sum_j A_{aj} = \rho_a \left(1 - \frac{qA}{E + \Delta}\right).$$ \hfill (C.11)

Summing (C.9) over the bonds $J$ gives then a relation which can be written

$$\mathcal{K} \rho_a = \delta \rho_a.$$ \hfill (C.12)

where

$$\mathcal{K} \rho_a = -\beta_a \Delta \sum_{b, \text{broken \sigma}} \rho_b$$ \hfill (C.13)

and

$$\varepsilon = -\frac{E + \Delta - \frac{qA}{E + \Delta} \times \left\{ (E + \Delta)^2 - \beta_\sigma^2 \right\} + p\Delta(E + \Delta)}{E + \Delta}.$$ \hfill (C.14)

$p$ is the number of saturated bonds $J$ per atom.

Equation (C.12) is the tight binding equation for an $s$ band on the atomic structure considered, with a negative transfer integral $-\beta_a \Delta$. To each self energy $\varepsilon$ of this problem, there correspond 3 solutions $E$. Thus the $s$ band, with two states per atom, gives rise to 3 sp bands, each with two states per atom.

General theorems give

$$-p\beta \Delta < \varepsilon < p\beta \Delta$$ \hfill (C.15)

where the upper limit is equal to $p\beta \Delta$ for alternant structures, but below $p\beta \Delta$ for non alternant structures.

With (C.13), these limits correspond to

$$E = \pm \beta_a - \Delta$$ \hfill (C.16)

and

$$E = \frac{A}{2} \left( q + p - 2 \pm \frac{\beta_a}{\Delta} + \varepsilon \sqrt{\left(q + p \pm \frac{\beta_a}{\Delta}\right)^2 + 4q \frac{\beta_a}{\Delta}} \right).$$ \hfill (C.17)

where $\varepsilon = \pm 1$. 

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The corresponding limits are pictured figures 14 to 16.
In the strong hybrid limit \( d \ll d_{\infty} \), a development of C.16 gives
\[
E = \frac{1}{2} \left[ \pm \beta_{s} + (q + p - 2) \Delta + \varepsilon \left[ \beta_{s} \mp (p - q) \Delta + \frac{2q \Delta^{2}}{\beta_{s}} + \ldots \right] \right] \quad (C.17)
\]

soit
\[
E_{1} = - |\beta_{s}| - (p - 1) |\Delta| - \frac{q \Delta^{2}}{|\beta_{s}|} + \ldots
\]
\[
E_{2} = - (q - 1) |\Delta| - \frac{q \Delta^{2}}{|\beta_{s}|}
\]
\[
E_{3} = - (q - 1) |\Delta| + \frac{q \Delta^{2}}{|\beta_{s}|}
\]
\[
E_{4} = |\beta_{s}| - (p - 1) |\Delta| + \frac{q \Delta^{2}}{|\beta_{s}|}.
\]

Finally the contribution of the various broad sp bands to cohesion could be computed, in the hybrid limit \( d \ll d_{\infty} \), by use of the density of \( \varepsilon \) states and its development in moments. However, for \( d \ll d_{\infty} \), a development of (C.13) for |\( E | \approx |\beta_{s}| \gg |\Delta| \) shows that the two broad (valence and conduction) sp bands are, in this limit, behaving in the same way as the valence and conduction bands of \( \sigma \) bonds with \( q = 0 \) and \( p \) neighbours, if one takes the same values of \( E_{0} \) and \( \Delta \) and if one neglects terms in \( \Delta^{2}/|\beta_{s}| \). To that order of perturbation, the middle of each sp band is therefore its center of gravity.

C. Flat bands. — Two particular solutions remain to be considered.

C.2.1 Cases of one broken bond per atom \( (q = 1) \).
— From equation (C.6), the condition
\[
\rho_{s} \equiv 0
\]
leads then necessarily to
\[
A_{sl} \equiv 0 \quad (C.20)
\]
Then equations (C.4), (C.5) give
\[
(E + \Delta) A_{sl} = \beta_{s} A_{bl}
\]
\[
(E + \Delta) A_{bl} = \beta_{s} A_{sl}.
\]
Hence
\[
E = - \Delta \pm \beta_{s}. \quad (C.21)
\]
These are the two flat \( \sigma \) bands (B, AB), also observed for \( \sigma \) bonding without broken bond. Indeed condition (C.20) shows that these bands have no amplitude on the broken bonds.

The degeneracies of these two bands must necessarily be equal. Their total degeneracy must be such that the total number of states per atom is 8. Hence the degeneracies marked figures 14 and 16 (i.e. degeneracy one for \( p = 3 \) and zero for \( p = 2 \)).

C.2.2 Case of two broken bonds per atom \( (q = 2) \).
— From equation (C.6), the condition
\[
E + \Delta = 0 \quad (C.22)
\]
leads necessarily to
\[
\rho_{s} \equiv 0 \quad (C.23)
\]
hence, from equation (C.4), (C.5), to
\[
A_{sl} \equiv 0 \quad (C.24)
\]
Conditions (C.23), (C.24) can be compatible with \( A_{sl} \neq 0 \), if there are more than one broken bond per atom (in practice, \( q = 2 \)). The corresponding flat sp\(^3\) band is marked figure 15.

Appendix D — Band structure for alternant structures. — Alternant structures are elementary structures where each atom has \( q \) equidistant first neighbours such that only closed circuits with an even number of interatomic jumps can be made.

As a result, the atomic sites can be divided into two families \( a, a' \ldots; b, b' \ldots \) such that each atom of one family has only atoms of the other family as nearest neighbours (Fig. D.1).

Fig. D.1. — Different types of alternant structures: a) simple cubic; b) body centred cubic; c) graphitic layer; d) diamond cubic lattice.

An electronic \( s \) band based on such a structure has then a density of states \( n(E) \) symmetrical in energy, if it corresponds to a Hamiltonian of the type
\[
H = \beta_{s} \left( \sum_{a \text{ near to } a} |a \rangle \langle b| + \sum_{a' \text{ near to } b'} |b' \rangle \langle a'| \right) + E_{s} \sum_{a \neq a, b} (|\alpha \rangle \langle \alpha|). \quad (D.1)
\]
This is a direct consequence of the fact that the odd moments are then zero:

\[ M_q = \int \rho(E) (E - E_s)^q \, dE \]

\[ = \frac{1}{N} \sum_{a \neq a', b} \langle a | (H - E_s)^q | a \rangle = \beta^q S_q. \]  

(D.2)

where \( S_q \) is the number per atom of closed circuits with \( q \) jumps.

This result extends directly to planar arrays of resonant \( \pi \) bonds. Owing to Leman, Thorpe and Weaire's theorem, it also provides a special symmetry for the broad sp bands corresponding to the sp hybrid Hamiltonian

\[ H = \beta_s \sum_{a, b} (| a, J \rangle \langle b J | + | b J \rangle \langle a J |) + \]

\[ + A \sum_{a \neq a', b, \pi, \sigma} | a J \rangle \langle a' J | + E_0 \sum_{a \neq a', b, \pi, \sigma} | a J \rangle \langle a' J |. \]  

(D.3)

A consequence of this symmetry property is that the top edges of the s and resonating \( \pi \) bands are exactly symmetrical from the bottom edges with respect to the atomic (s or p) energy. The exact edges of the sp band gap could also be deduced from this fact.

Another way of obtaining this result gives a further insight into the band structure. It shows in particular that the density of states should, in some cases, go to zero in the middle of the band. This reasoning, as the preceding one, does not necessarily imply a crystal structure, although the practical applications will be on crystals.

D.1 s bands. — Writing that

\[ | \psi \rangle = \sum_{a, b} A_a | a \rangle \]  

(D.4)

is an eigenfunction of \( \mathcal{H} \) given by (D.1), we obtain

\[ (E - E_s) A_a = \beta_s \sum_{b \text{ near } a} A_b \]  

(D.5)

\[ (E - E_s) A_{a'} = \beta_s \sum_{a' \text{ near } b} A_a. \]  

(D.6)

We substitute (D.6) into (D.5), taking into account that each b atom has one neighbour which is a and \( (q - 1) \) neighbours which are not a:

\[ (E - E_s)^2 A_a = \beta_s^2 \sum_b \left( A_a + \sum_{a' \neq a} A_{a'} \right). \]  

(D.7)

If each atom has \( q_1 \) first neighbours and if each site \( a' \) can be reached from a in two jumps through \( q_2' \) first neighbours b, (D.7) can be written

\[ [(E - E_s)^2 - q_1 \beta_s^2] A_a = \beta_s^2 \sum_{a'} q_2' A_{a'}. \]  

(D.8)

Comparing with (D.5), the coefficients \( A_a \) are those of the development of the eigenfunctions of an s band for the structure of the a sublattice, with equal transfer integrals

\[ B' = -\beta_s^2 \]  

(D.9)

between each site a and a set of neighbours \( a' \) reached from a by two jumps through a b atom and an energy

\[ \varepsilon' = q_1 \beta_s^2 - (E - E_s)^2. \]  

(D.10)

Similar results would hold with the \( A_a \) coefficients.

This theorem has the following consequences:

D.1.1 It is sufficient to study the s band of problem (D.9) for the sublattice a. For simple cubic and diamond cubic structures, this is an FCC lattice; for a BCC structure, it is a simple cubic lattice; for a graphitic layer, it is a close packed triangular layer (Fig. D.1).

D.1.2 For each value of \( \varepsilon' \), there are two values of \( E \), symmetrical with respect to \( E_s \). Thus as stated above, the density of \( E \) states is symmetrical with respect to \( E_s \), and so are in particular the two band edges.

D.1.3 From general theorems, the ground state of \( \varepsilon' \) is obtained, in a macroscopic aggregate, when the corresponding wave function has equal values on all sites a : \( A_a = \text{const.} \), for this minimizes the kinetic energy. Thus

\[ \varepsilon' \geq E_1 = QB \]  

(D.11)

where \( B \) is the (negative) transfer integral (D.9) and \( Q \) is the number of \( a' \) sites associated with each a site, each taken with its degeneracy \( q_2' \).

| Table D.I |
|--------------------------|--------------------------|
| \( q_1 \)               | \( Q = \sum q_2' \)   |
| Simple Cubic            | 6                        | 30                      |
| BBC                     | 8                        | 56                      |
| Graphitic layer          | 3                        | 6                       |
| Diamond Cubic           | 4                        | 12                      |

\[ Q = \sum q_2' = q_1(q_1 - 1). \]  

(D.12)

Equations (D.10), (D.11), (D.12) lead to the exact well known limits

\[ q_1 \beta_s \leq E - E_s = - q_1 \beta_s. \]  

(D.13)

Now, in some special alternant structures, all the \( a' \) atoms. reached from a by two jumps through a b atom, are nearest neighbours to a in the sublattice. This is true in the graphite layer and the diamond cubic and hexagonal lattices, because they are build...
with large rings; it is not true for the more compact simple cubic or BCC structures (Fig. D.1).

For these special structures, the transfer integral $B$ in the $s$ band of the $a$ sublattice only connects nearest neighbors $a$, $a'$ in the $a$ sublattice (equation D.8), and well known results for the upper limit of $\varepsilon'$ can be applied. In all three cases, the $a$ sublattice is a non alternant lattice, so that the upper limit to $\varepsilon'$ is below $-QB = q_1(q_1 - 1)\beta_s^2$. This would indeed correspond to an imaginary value of $E$. In fact, in all three cases, the upper limit of $\varepsilon'$ is

$$\varepsilon' \leq \varepsilon'_2 = - q_1 B = q_1 \beta_s^2. \quad (D.14)$$

This upper limit corresponds to

$$E = E_\ast \quad (D.15)$$

where the two $E$ subbands just touch.

If near $\varepsilon'_2$, the density of $\varepsilon'$ states varies as

$$n(E) = n(\varepsilon') \frac{d\varepsilon'}{dE} \propto (\varepsilon'_2 - \varepsilon')^2. \quad (D.16)$$

then the corresponding density of $E$ states varies as

$$n(E) = n(\varepsilon') \frac{d\varepsilon'}{dE} \propto (E - E_\ast)^2. \quad (D.17)$$

For the triangular closepacked sublattice associated with a graphitic layer (Fig. D.1c), and for the FCC sublattice associated with the diamond cubic structure (Fig. D.1d), $\mu = 0$ and $-\frac{1}{2}$ respectively, as shown by expansion of $E(k)$ around $k = (4\pi/3\ a, 0)$ and $(2\pi/a, 0, 0)$ respectively.

Thus the two subbands $n(E)$, for $E \geq E_\ast$, meet with a constant value of $n(E_\ast)$ for the diamond cubic lattice, and also for the diamond hexagonal, owing to the identity of $n(\varepsilon')$ for the FCC and HCP $s$ bands structures. But $n(E)$ goes to zero with a finite slope $(dn/dE)$ at $A = E_\ast$ (Fig. D.2) for the graphite layers.

D.2 $\pi$ bands of graphitic layers. — The preceding analysis applies directly to the $\pi$ bands of graphitic layers, replacing $E_i$ by $E_\pi$ and $\beta_i$ by $\beta_\pi$ (also negative).

In graphite ($z = 4$ valence electrons per atom), there is one $\pi$ electron per atom. The $\pi$ band is half full. Thus the lower subband $E \leq E_\pi$ is full, and the top one $E \geq E_\pi$ empty; the Fermi level falls at the energy $E_\pi$ where the Fermi surface is reduced to a collection of points in reciprocal space. This is a well known feature of such layers in this approximation. It stabilizes somewhat the graphite structure by lowering the average energy in the lower half of the $\pi$ band.

D.3 Broad $sp$ bands in $sp^6$ hybrid structures. — Leman, Thorpe and Weaire's theorem shows that the tight binding Hamiltonian $H$ for an alternate structure (D.3) leads to an effective $s$ band problem on the same lattice.

$$\varepsilon(\rho) = B \sum_{\beta \text{ near to } a} \rho_\beta \quad (D.18)$$

where $a$ and $\beta$ are $a$ or $b$ sites

$$B = - \beta_\sigma A \quad (D.19)$$

$$\varepsilon = \beta_\sigma^2 - (E - E_0 + A)^2. \quad (D.20)$$

From the analysis of the $s$ band problem.

D.2.1 Diamond cubic and hexagonal structures will have a density of $E$ states $\varepsilon(\varepsilon)$ which is finite and continuous at the center $\varepsilon = 0$ of the band. Thus the density of $E$ states $n(E)$ will go to zero linearly with $E$ at energies

$$E_m = E_0 - \Delta \pm \beta_\sigma. \quad (D.21)$$

D.2.2 Graphitic layers will have a density of $E$ states $\varepsilon(\varepsilon)$ which goes to zero linearly with $E$ at $E = 0$. Thus the density of $E$ states $n(E)$ will go to zero parabolically with $E$ at energies $E_m$ given by (D.21).

In both cases, the energies $E_m$ separate each of the broad $sp$ ($\sigma$) bands into two subbands with one electron per atom. This would stabilize somewhat the corresponding structures for $z = 1$ and 5. In practical cases however ($z = 4$), the lower $\sigma$ band is full and the upper one empty. Thus their splitting has no special effect on cohesion.
References