In terms of the relative momentum $\mathbf{P}_{32}$; $\mathbf{P}_{32}$ must be within a solid angle $\pi R^2/|\mathbf{r}_{23}(t')|^2$ in the direction $\mathbf{r}_{23}(t')$, which at large distances can be replaced by $\pi R^2/|\mathbf{r}_{12}(t')|^2$, where $\mathbf{r}_{12}(t') = \mathbf{r}_{12} - \mathbf{P}_{12}t'/m$ and $\mathbf{r}_{12} = \mathbf{q}_1 - \mathbf{q}_2$, $\mathbf{P}_{12} = \mathbf{p}_1 - \mathbf{p}_2$.

In (B1) changing the momentum integration to $\mathbf{P}_{32}$ we have

$$\int_0^t dt' \int d\Omega_{P_{32}} \alpha,$$

$$\alpha = -\frac{1}{v} \int d\mathbf{q}_3 dP_{32} P_{32}{}^2 \frac{\partial \varphi_{13}}{\partial \mathbf{q}_1} \cdot \frac{\partial F_1}{\partial \mathbf{p}_1} g^{(1)}.$$

(B2)

To obtain the magnitude of (B2) we neglect the variation of α with time and treat it as constant with respect to the angles when it is nonzero. We then have

$$\alpha \int_0^t dt' \frac{\pi R^2}{|\mathbf{r}_{12}(t')|^2}$$

$$= \frac{\alpha \pi R^2}{r_{12}(P_{12}/m)(1-\cos^2\theta)^{1/2}} \left\{ \tan^{-1}\left[\frac{P_{12}t/mr_{12} - \cos\theta}{(1-\cos^2\theta)^{1/2}} \right] \right.$$

$$\left. - \tan^{-1}\left[\frac{-\cos\theta}{(1-\cos^2\theta)^{1/2}} \right] \right\}, \quad \text{(B3)}$$

where θ is the angle between $\mathbf{r}_{12}$ and $\mathbf{P}_{12}$. Equation (B3) approaches a limit as $t \to \infty$, according to

$$\frac{\alpha \pi R^2}{r_{12}(P_{12}/m)(1-\cos^2\theta)^{1/2}} \left\{ \frac{\pi}{2} - \tan^{-1}\left[\frac{-\cos\theta}{(1-\cos^2\theta)^{1/2}} \right] \right.$$

$$\left. - \frac{(1-\cos^2\theta)^{1/2}}{P_{12}t/mr_{12}} \right\}. \quad \text{(B4)}$$

Possibility of Synthesizing an Organic Superconductor*

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London's idea that superconductivity might occur in organic macromolecules is examined in the light of the BCS theory of superconductivity. It is shown that the criterion for the occurrance of such a state can be met in certain organic polymers. A particular example is considered in detail. From a realistic estimation of the matrix elements and density of states in this polymer it is concluded that superconductivity should occur even at temperatures well above room temperature. The physical reason for this remarkable high transition temperature is discussed. It is shown further that the superconducting state of these polymers should be distinguished by certain unique chemical properties which could have considerable biological significance.

I. INTRODUCTION

IN the forward to Vol. 1 of his monographs on superfluids, F. London[1] questions whether a superfluid-like state might occur in certain macromolecules which play an important role in biochemical reactions. If this should be the case, an entirely new and important consideration would be added to the problem of understanding living systems. In view of the significance of such an effect, it appears appropriate at this time, when a theory of superconductivity, the Bardeen-Cooper-Schrieffer (BCS) theory[2] has been so remarkably successful in explaining much of the behavior of superconductors, to examine in the light of this whether or not a superconducting state might occur in certain macromolecules. In view of the extreme complexity of biological systems, it would be folly for a physicist to

attempt to experiment in such an environment. Instead of attempting this, we shall tackle the problem on our own grounds. The BCS theory, while by no means complete and exact, has succeeded in providing a model with most of the essential features of a superconductor. In particular, it prescribes certain criteria for a system which, if satisfied, should lead to the superconducting state. Our approach is to consider how these criteria might be applied to the design of a particular organic molecule which, if its synthesis is possible, should show some of the essential features of a superconductor and, as we shall show, some remarkable chemical properties as well. One of the interesting features about the particular class of molecules we investigate in detail is that the molecules should be superconducting at room temperature and, indeed, to temperatures well above room temperatures. We can show on simple physical grounds why this is so and perhaps, with hindsight, why this was to be expected.

The idea of superconductivity in organic systems is not a new idea, however, there is a considerable amount

[1] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1.

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

of confusion as to the exact meaning of this. The diamagnetic ring currents of aromatic molecules such as benzene, naphthalene, etc., are nondissipative currents similar in many respects to the persistent currents of superconducting rings and, have often been referred to as a form of superconductivity. However, the "superconductivity" of these molecules is not the same as the superconductivity of bulk materials. The reason, I believe, is the following. In macroscopically large superconductors, if superconductivity exists, then a finite fraction of the charge carriers, in general, the BCS pairs are in identically the same center-of-mass momentum state. This state then has a macroscopic occupation. In a magnetic field the canonical momentum of this state remains unchanged, but due to the vector potential term contained in it a current is induced and the energy of the state changes. For a macroscopically large superconductor the kinetic energy of the different center-of-mass momentum states of the pairs lie extremely close to one another, however, because the coherence energy of each state depends upon the square of the number of pairs in that state, the state which is macroscopically occupied is appreciably lower in energy than any of the neighboring states even in a moderate magnetic field. It is only by transitions in which practically all the pairs in the macroscopically occupied state simultaneously move to another state that a lower energy final state can be reached. This is obviously highly forbidden and, consequently, the system of pairs remains in the momentum state into which condensation originally occurred. Thus, it is the coherence energy which prevents the system from freely adjusting itself to take the lowest possible energy. In the aromatic ring compounds practically all the molecules are in their ground states. In a magnetic field the canonical momentum of the electrons in this state remain unchanged and diamagnetic currents flow in the molecule similar to those of a bulk superconductor. The energy of the different momentum states of the electrons in each molecule in this case are well separated though, because the molecules are of microscopic size. Thus, the momenta of the electrons do not change because for fields as large as those available in the laboratory, the state which evolves out of the original ground state still is lower in energy than any other in the presence of the field. If, however, the aromatic system is made arbitrarily large such as in graphite, bulk superconductivity does not result because as the system gets bigger, the different momentum states of the electrons approach each other in energy. Transitions can then occur between states and the induced currents are dissipated. So that in order to get superconductivity in a macromolecule or in a bulk material, something of the nature of a coherence energy is required. In conventional superconductors this is provided by the phonon-induced, electron-electron interaction; in attempting to devise a macromolecule which is to be superconducting

one must provide, therefore, some mechanism similar to this. In our model we do this in the following manner.

II. MODEL SYSTEM

We shall consider a molecule consisting of two parts, a long chain called the "spine" in which electrons fill the various states and may or may not form a conducting system; and secondly, a series of arms or side chains attached to the spine as indicated in Fig. 1. We will show that by appropriate choice of the molecules which constitute the side chains, the virtual oscillation of charge in these side chains can provide an interaction between the electrons moving in the spine. This can be made a sufficiently attractive interaction so that the superconducting state results. We can show further that even if the spine by itself is initially an insulator due to the valence band being full and the conduction band empty, the addition of side chains can increase the electron-electron attraction to the point where it becomes energetically favorable to enter the superconducting state by mixing in states of the conduction band. The spine thus transforms from the insulating or semiconducting state directly to the superconducting metallic state upon the addition of the side chains.

Consider a long chain molecule as shown in the left half of Fig. 1. We will assume this is a conjugated chain of double and single bonds resonating between the two at each link. This corresponds in the band theory of metals to a band which is half filled and ideally is a metallic conductor. (See, however, Sec. III.) At the points P, P', $\cdots$, a regular array of side chain molecules B are attached. The individual side-chain molecules are chosen to have a low-lying excited state such that transitions from the ground state to the excited state correspond classically to an oscillation of charge from end to end of the molecule.

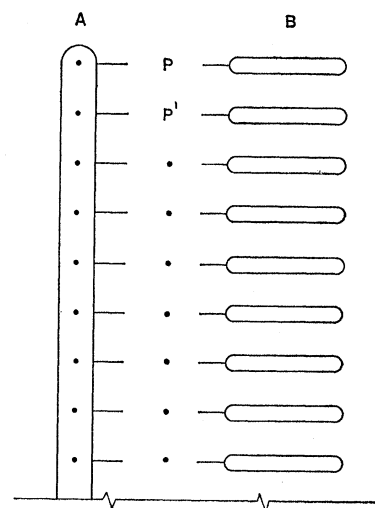The electrons moving in the spine may be described

FIG. 1. Proposed model of a superconducting organic molecule. The molecule A is a long unsaturated polyene chain called the "spine." The molecules B are side chains attached to the spine at points P, P', ⋯.

in the tight-binding approximation[3] by eigenfunctions of the form

$$\phi_{k,m}(r) = \frac{1}{G^{1/2}} \sum_i e^{ikR_i} U_m(r-R_i), \qquad (2.1)$$

where $U_m(r-R_i)$ is the wave function of an electron in a single atom located at R_i. G is the number of links in the chain and ϵ_k is the energy of this electron and we will assume cyclic boundary conditions. To avoid unnecessary complication we shall ignore the electron spin throughout the discussion except where necessary.

The wave function of the electrons in a single side-chain molecule in an eigenstate n we designate by $\psi_n(r_1, r_2, \cdots)$. Due to the interaction of one side chain upon its neighbors, the degeneracy of the levels of the group of side chains will be removed when the side chains are brought together as in Fig. 1. The band of levels of the system of side chains as a whole can be described then by a new wave function similar to (2.1) above.

$$X_{q,n} = \frac{1}{G^{1/2}} \sum_j e^{iqR_j}\psi_n(r_1-R_j; r_2-R_j\cdots). \quad (2.2)$$

The Coulomb interaction between the electrons in the spine and those on the side chain will provide an interaction between the electrons in the spine and the side-chain modes. Let this Coulomb interaction be $V_1 = \sum_{i,j} V(r-R_i; r_1-R_j, r_2-R_j, \cdots)$ which will give rise to a typical interaction matrix element

$$\int\int \cdots \int \phi_{k'm'}{}^*(r) X_{q'm'}{}^*(r_1, r_2\cdots)$$
$$\times V_1 X_{qn}(r_1, r_2\cdots)\phi_{km}(r)d^3r d^3r_1\cdots. \quad (2.3)$$

In the model we shall consider, screening reduces the range of the Coulomb interaction so that one can safely disregard the contribution to the interaction from any but the neighboring side chains. Secondly, in our model there is negligible overlap between side chains, and also overlap between sites on the spine is relatively small. These features together with the properties of (2.1) and (2.2) and the assumption of regular substitution along the spine allow us to approximate the interaction (2.3) to give the following

$$V_{k'm',q'n',qn,km} = \frac{1}{G} \sum_{n''=-1,0,+1} \cos Qn''a \int \cdots$$

$$\times \int U_{m'}{}^*(r)\psi_{n'}{}^*(r_1-n''a, \cdots)$$

$$\times V_1\psi_n(r_1-n''a)U_m(r)\times d^3r d^3r_1\cdots, \quad (2.4)$$

where $k'=k+Q$, $q'=q-Q$, and a is the spacing between side chains.

It is convenient to write this as $(1/G)V(Q)$ for the moment. Then the complete spine side-chain interaction can be described in the representation of second quantization as

$$V_{\text{side chain}} = \frac{1}{G} \sum_{\substack{Q,n,n' \\ k,m,m'}} V(Q)(\sum_q c_{q-Q,n'}{}^\dagger c_{q,n})a_{k+Q,m'}{}^\dagger a_{km}, \quad (2.5)$$

where the $a^\dagger$ and a are the creation and destruction operators for the electron in the spine, and $c^\dagger$ and c the corresponding operators for the side-chain modes. The particle-hole operator $\sum_q c_{q-Q,n'}{}^\dagger c_{qn}$ which occurs in (2.5) appears in a similar manner to the phonon creation operator $b_Q{}^\dagger$ in the phonon-electron interaction in a metal. The terms linear in this particle-hole operator which appear through the interaction (2.5) in the total Hamiltonian can be eliminated by the same type of transformation[4] which eliminates the terms linear in the phonon creation operator $b_Q{}^\dagger$ in the conventional theory. This leads to a side-chain induced electron-electron interaction V_2 *between* electrons in the spine of the form

$$V_2 = \frac{1}{2} \sum_{k,k',Q} \left\{ \frac{2V^2(Q)}{G} \frac{\hbar\omega_Q}{(\epsilon_{k+Q}-\epsilon_k)^2 - (\hbar\omega_Q)^2} \right\}$$
$$\times a_{k+Q}{}^\dagger a_{k'-Q}{}^\dagger a_{k'} a_k. \quad (2.6)$$

We have written $\hbar\omega$ for the difference $(E_{n'}-E_n)$ between the energy of the states of the side-chain modes and have considered for simplicity only one excited state n'. This is identical in form to the usual phonon-induced electron-electron coupling. We note that if $|\hbar\omega| \gg |(\epsilon_{k+Q}-\epsilon_k)|$ then the term in brackets reduces to an attractive interaction, $V \approx -2\langle|V(Q)|^2\rangle_{\text{av}}/G\hbar\omega$, where $\langle|V(Q)|^2\rangle_{\text{av}}$ is the average of the square of the interaction $V(Q)$.

In addition to this attractive term, the screened Coulomb interaction gives a repulsive term. The sum of these two is the net electron-electron interaction. Let this sum be $\langle V(Q)\rangle_{\text{av}}$; then the total Hamiltonian for the electrons in the spine is

$$\mathcal{H} = \sum_k (\epsilon_k - \mu)a_k{}^\dagger a_k$$
$$+ \frac{1}{2} \sum_{k,k',Q} \langle V(Q)\rangle_{\text{av}} a_{k+Q}{}^\dagger a_{k'-Q}{}^\dagger a_{k'} a_k, \quad (2.7)$$

where $\langle V(Q)\rangle_{\text{av}}$ is given above and μ is the Fermi energy.

The BCS theory then shows that a superconducting state is possible if the following equation can be satisfied for a nonzero gap, Δ:

$$-1 = \sum_k \frac{V \tanh\frac{1}{2}\beta E_k}{2E_k}, \quad (2.8)$$

[3] See for example N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936).

[4] J. Bardeen, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 15, p. 352.

where $E_k = [(\epsilon_k - \mu)^2 + \Delta^2]^{1/2}$ and the sum is limited by $|\epsilon_k - \mu| < \hbar\omega$. V is the average over the region of Q where $\langle V(Q) \rangle_{av}$ is attractive. The critical temperature is given by

$$kT_c = 1.14\hbar\omega \exp[-1/N(0)V], \qquad (2.9)$$

where $N(0)$ is the density of states of one spin at the Fermi surface.

It is appropriate to dispose of a difficulty here which will arise shortly in considering a particular example of a molecule. In long-chain conjugated molecules the double and single bonds do not resonate freely between each position in the chain, but tend to localize so that a stationary periodic charge distribution and periodic bond length is established. This introduces a periodic potential of twice the atomic spacing in the chain which in turn produces a gap in the density of states halfway up the band. As there is one electron per atom in the band, this band is filled up to the new gap. The conjugated system is then no longer a metallic conductor but a semiconductor or insulator, i.e., the density of states at the Fermi surface $N(0)$ would be zero.[5] However, it is incorrect to interpret Eq. (2.9) as indicating that $T_c = 0$ in this case, for Eq. (2.9) is only an approximation. Instead, one must go back to (2.8) and examine this to see whether in this case a solution is possible. In the next section we consider this in detail.

III. SUPERCONDUCTIVITY IN A SEMICONDUCTOR

Let us consider a somewhat idealized case of a semiconductor with a band structure as shown in Fig. 2. Before the introduction of the periodic potential which generates the gap, the energy of the states would have been given by that shown by the dashed line in the figure. Let us take the band gap as δ and for convenience we will assume the density of states near the band edge is the same in the two bands. If the lower band is completely filled and the upper empty, then the Fermi level will be halfway between the two bands. We will assume that $\hbar\omega$ is greater than δ.

Let $N(0)$ be the density of states at the Fermi surface for the system prior to the introduction of the periodic potential and let ϵ be the energy of these states measured with respect to the Fermi surface. The semiconductor band gap can then be conveniently introduced by changing the energy of each state ϵ to $\epsilon' = [\epsilon^2 + (\delta/2)^2]^{1/2}$. We can now use Eq. (2.8) to see if the superconducting state can occur at any temperature. At $T = 0°K$ a

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[5] Where one does not have alternating double and single bonds, but a double bond separated from the next by two single bonds, the band theory does not appear to work and one finds that the chain is an insulator instead of a metal. This empirical fact does not appear to have been explained, but seems to be a consequence of the same considerations of the metallic and insulating states discussed by N. F. Mott [Phil. Mag. **6**, 287 (1961)], and W. Kohn [Phys. Rev. **133**, A171 (1964)]. As this question is not quite settled we have limited ourselves to a conjugated chain which is known to behave as one would expect from the band theory.
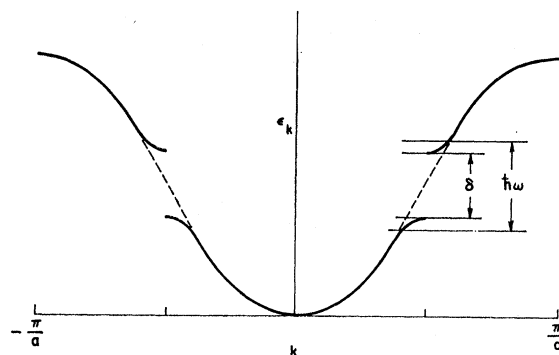

FIG. 2. Band structure of a conjugated chain semiconductor caused by the localization of the double bond. The energy $\hbar\omega$ is the energy of the transitions of the side chains.

superconducting state is possible if V is negative and

$$1 < \sum_\epsilon \frac{|V|}{2[\epsilon^2 + (\delta/2)^2]^{1/2}}, \qquad (3.1)$$

where the sum is limited by $|\epsilon'| < \hbar\omega$.

Transforming to an integral, we require

$$\frac{1}{N(0)|V|} < \int_0^x \frac{d\epsilon}{[\epsilon^2 + (\delta/2)^2]^{1/2}}, \qquad (3.2)$$

where $x^2 = (\hbar\omega)^2 - (\delta/2)^2$ and $N(0)$ is defined above prior to the introduction of the gap.

$$\frac{1}{N(0)|V|} < \ln\left[\frac{[(\hbar\omega)^2 - (\delta/2)^2]^{1/2} + \hbar\omega}{\delta/2}\right]. \qquad (3.3)$$

If $(\delta/2)^2 \ll (\hbar\omega)^2$ then the criterion for obtaining the superconducting state is that

$$\delta < 4\hbar\omega \exp\left[\frac{-1}{N(0)|V|}\right]. \qquad (3.4)$$

If this criterion can be satisfied, then the transition temperature can be obtained from the expression

$$\frac{1}{N(0)|V|} = \int_0^x \frac{\tanh\frac{1}{2}\beta_c\epsilon'}{\epsilon'} d\epsilon, \qquad (3.5)$$

which is the same expression for determining the temperature at which the energy gap of a superconductor becomes equal to $\delta/2$. The form of this expression is given graphically in the BCS paper. We only need note that T_c rapidly approaches the transition temperature for $\delta = 0$ as $|V|N(0)$ is increased beyond that necessary to satisfy the criterion. So that if the criterion can be satisfied, then the transition temperature generally will be of the same order as the transition temperature of the metallic superconductor. We see then that a gap in the band structure does not necessarily exclude the superconducting state. Incidentally, this conclusion does

not violate Yang's[6] statement that superconductivity or off-diagonal-long-range order (ODLRO) cannot occur in an insulator because his definition of an insulator is one in which there are no available empty states. Our point is that these states are, in fact, available in our model.

It is perhaps appropriate to note that a gap in the density of states such as that considered above would make the average side-chain induced interaction more strongly attractive because for interband transitions $(\epsilon_{k+Q} - \epsilon_k)$ would be at least δ and as can be seen from (2.6), the attractive term would thus become larger provided that $\delta < \hbar\omega$. If one takes the variation of $\langle V(Q) \rangle_{av}$ with Q into account, the details of the above inequality are, of course, changed, but the general feature that the existence of superconductivity is determined by some such criterion remains.

IV. PARTICULAR EXAMPLE

As a particular example of a molecule of the type considered in Sec. II, we will consider in detail the molecule illustrated in Fig. 3. The spine is a conjugated chain of alternating double and single bonds. To this is attached a series of side-chain molecules as shown. Because of the great thickness of the benzene rings in the side chains, compared to the carbon-carbon spacing in the spine, it is not possible to attach a side chain to every carbon atom on the spine. This can be seen more clearly in Fig. 4 where the molecule is drawn to scale using the known values for the van der Waals radii of the constituent atoms. The changed periodicity of the new structure necessitates a slight modification of the wave function used in (2.1) and (2.2) above, but the modification is an obvious one which we will handle later. The side-chain molecule is part of a well-known dye molecule used for sensitizing photographic plates in the red, a diethyl-cyanine iodide, and it has been
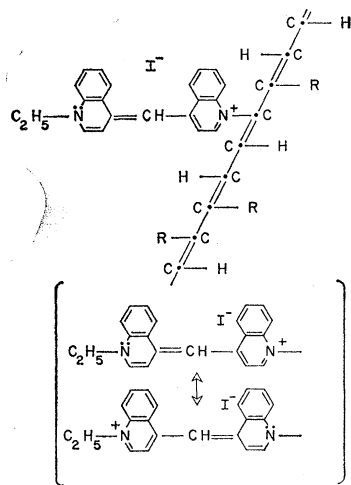
FIG. 3. Chemical structure of the proposed superconducting organic polymer. At each point R on the spine a similar side chain to the one shown is attached. These side chains are resonating hybrids of the two extreme structures shown in the inset. The positive charge resonates between the two nitrogen sites as illustrated.

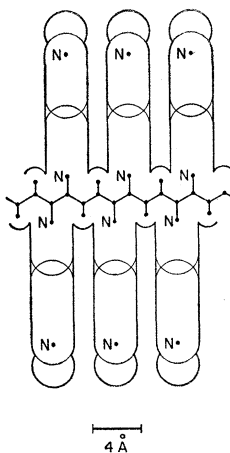[6] C. N. Yang, Rev. Mod. Phys. 34, 694 (1962).

FIG. 4. Approximate scale drawing of the proposed superconducting organic polymer. The plane of the benzene rings in the side chains are oriented at right angles to the spine. The two nitrogen sites on each side chain are indicated, but the iodine site has been omitted for the sake of clarity.

chosen because its absorption spectrum is known, and its ground and excited states are well understood.[7]

Before estimating the matrix elements of the interaction of the side chains with the electrons in the spine, it is useful to consider first what effect screening will have upon the Coulomb interaction.

Screening

The Coulomb potential at a distance r from a charge which is placed in a conducting medium is screened by the rearrangement of the charges of the medium. The potential is then given approximately by $(e/r)e^{-\lambda r}$. The screening length $1/\lambda$ in a free-electron gas can be estimated by using the Thomas-Fermi method as shown by Mott and Jones.[4] From this one finds that $\lambda^2 = (4me^2/\hbar^2)(3N_0/\pi)^{1/3}$ where N_0 is the number of electrons per unit volume. For the carbon atoms on the spine, one valence electron per atom is relatively free, and from the known size of the atom one can estimate N_0 and thus λ. We find that $1/\lambda$ is approximately 0.5 Å. This value varies extremely slowly with the number of valence electrons so that our choice of one free valence electron is not critical. We note then that the Coulomb interaction is screened out in an extremely short distance.

It should be noted too that screening can occur only where the charges of the medium are free to move, as for example, within an atom or along the conjugated series of atoms of the spine. Where the charges are not free to move indefinitely, then only a limited displacement of the charges occurs which merely modifies the Coulomb interaction by the dielectric constant of the medium, but does not screen it. These two cases must be born in mind in considering the Coulomb interaction and the side-chain interaction. Because the electrons are free to move in the spine one must use the screened Coulomb interaction for computing the Coulomb repulsion between the electrons in the spine. However,

[7] K. Mees, The Theory of the Photographic Process (The Macmillan Company, New York, 1942), p. 987.

the interaction between the electrons in the spine and the charges on the side chain is only partially screened because the side chain is insulated from the spine and a free movement of charge between the two cannot occur, i.e., the conjugation of the side chain does not extend to the spine. Here one must use the Coulomb interaction modified by the dielectric constant of the medium together with some screening due to the induced movement of charge in the spine.

Coulomb Repulsion

For steric reasons, it is not possible to attach a side chain to each carbon atom of the spine. Consequently, the Hamiltonian of the spine is not invariant under a displacement from one atom to the next as assumed in our earlier discussion. In our example, the unit cell is repeated only after four carbon atoms and thus, we are dealing here with a lattice with a basis of four atoms. The wave function of the spine is then

$$\phi_{km} = \frac{1}{(G)^{1/2}} \sum_{i}^{G} e^{ikR_i} \sum_{j=1}^{4} \alpha_{kj} U_m(r - r_{j,i}). \quad (4.1)$$

R_i is now the position of the lattice point measured along the zig-zag line joining the carbon atoms and $r_{j,i}$ the position of the jth atom in the unit cell measured with respect to R_i. α_{kj} is a phase factor which one would expect would be very nearly $(1/4^{1/2})e^{ik(r_{j,i})}$, which is the value it would have if the Hamiltonian was perfectly invariant under a C$-$C displacement. The number of unit cells, G is now a quarter of the number of carbon atoms in the spine.

Let us now calculate the Coulomb repulsion between electrons in states given by (4.1):

$$V(Q)_{\text{Coulomb}} = \int \int \phi_{k-Q}^*(r_1)\phi_{k'+Q}^*(r_2)V(r_{12})$$
$$\times \phi_{k'}(r_2)\phi_k(r_1)d^3r_1 d^3r_2. \quad (4.2)$$

Using (4.1) and the fact that the Coulomb interaction is screened from all except immediate neighboring ions, we obtain in the long-wave limit, i.e., $Q \approx 0$

$$V(0)_{\text{Coulomb}} = \frac{1}{4G}\bigg[\int |U(r_1-r_j)|^2 V(r_{12})|U(r_2-r_j)|^2 d^3r_{12}$$
$$+ \sum_{k=j\pm1} \int |U(r_1-r_j)|^2 V(r_{12})|U(r_2-r_k)|^2 d^3r_{12} \bigg]. \quad (4.3)$$

The second term should be much smaller than the first because $V(r)$ is heavily screened. To a first approximation we shall ignore it compared to the first. A reasonable exact value of the dominant term could be obtained by using the known form of the sp carbon orbital and evaluating the integral, however, one can obtain a reasonable estimate of the approximate magnitude of the term by considering the electron density in the orbital as constant and occupying a volume of about

half the volume of the atom. The integral is easily done and gives $6e^2/\lambda^2 R^3$ where R is the van der Waals radius of the carbon atom. Using the value obtained above for λ and a van der Waals radius of 1.5 Å[8] we obtain a value of 6 eV for the integral. This seems to be a reasonable estimate for one might expect it to be comparable to the energy necessary to add one additional electron to a carbon atom. The energy necessary to form the C$^-$ ion is known as the electron affinity A and is related to the ionization energy I and the electronegativity x of the atom by the relation[8] $(I+A)/5.4 = x$ where I and A are expressed in electron volts. The ionization energy of carbon is 11.3 eV and x is 2.5 giving an electron affinity for carbon of 2.2 eV. This is of the same order of magnitude estimated above. Taking the larger value of 6 eV to be safe we find

$$V(0)_{\text{Coulomb}} \approx 1.5 \text{ eV}/G. \quad (4.4)$$

For larger values of Q the first term in (4.3) remains unchanged in the tight-binding approximation while the second term which we have neglected above is reduced by an additional factor of $\cos Qa$ where a is the carbon-carbon spacing. Over the whole range of Q, then we can take the Coulomb repulsion to be of the order of that given by (4.4)

Side-Chain Interaction

The wave function of the side chain must be modified in the same way as the wave function for the electrons of the spine. It is now

$$X_{qn} = \frac{1}{G^{1/2}} \sum_{i=1}^{G} e^{iqR_i} \sum_{j=1}^{4} \beta_{q,j}\psi_n(r - r_{j,i}, \cdots). \quad (4.5)$$

At the sites, j, where side chains are attached β is approximately $e^{iqr_{ji}}/2^{1/2}$, and zero where there are no side chains.

The side chain we have chosen is a resonating hybrid of the two extreme structures shown in the inset to Fig. 3. If the wave functions of these two extreme structures are ψ^+ and ψ^-, respectively, then the ground state, ψ_0 is $(1/\sqrt{2})(\psi_+ + \psi_-)$ and the excited state of interest to us, ψ_1 is the orthogonal hybrid structure $(1/\sqrt{2})(\psi_+ - \psi_-)$. In the matrix element (2.4) we require $\psi_1^*\psi_0$ which is simply $\frac{1}{2}[|\psi_+|^2 - |\psi_-|^2]$.

Using the new wave functions for the spine (4.1) and (4.5), Eq. (2.4) reduces to

$$V(Q)_{\text{side chains}} = \int \int \sum_{j=1}^{4} \sum_{n=-1}^{+1} \alpha_{k+Q,j}^* \alpha_{kj} |U_m(r - r_{ji})|^2$$

$$\times V(r)e^{iQn4a}\frac{1}{2}\sum_{l=1}^{4} \beta_{q+Q,l}^* \beta_{q,l}$$

$$\times \{ |\psi_+(r_{l,i+n})|^2 - |\psi_-(r_{l,i+n})|^2 \}, \quad (4.6)$$

[8] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), pp. 257, 95.
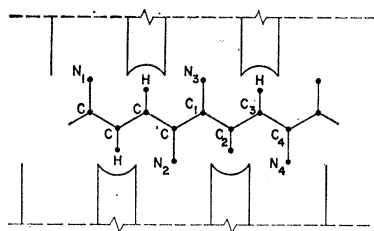
FIG. 5. Enlarged view of atoms of the spine of the proposed polymer.

where we have confined ourselves to a single atomic level m. The different k levels then describe the bands of the type discussed in Sec. III. We recall that j and l refer to each of the four atomic sites within the unit cell; and n has values 0 and ± 1 which refer to the same unit cell, i and the two adjacent cells, respectively.

In the superconducting state two types of matrix elements are important; those which describe scattering between states close to the Fermi surface with momentum transfer $Q \approx 0$ and those for scattering from one side of the Fermi surface to the other. The latter scattering involves a $Q \approx \pi/a$ because there is one electron per atom in the band originating from the fourth sp_3 orbital of the carbon atom. We shall estimate the side-chain interaction matrix element in the neighborhood of these values of the momentum transfer.

Firstly, the interaction between the spine and the iodine ion of the side chain cancels in the matrix element (4.6) because the ion is located at the same point in the two extreme structures of the hybrid. Secondly, in the ψ_- structure the positive charge is located on the nitrogen site which is remote from the spine, consequently, the interaction with this structure is weak. The only important contribution to the matrix element then, is that which is due to the positive charge on the nitrogen close to the spine in the ψ_+ structure, and the electron on each of the sites r_j.

In Fig. 5 we show an enlarged drawing of the spine and part of the side chains. In view of our earlier discussion of screening, it would be consistent to treat the interaction between the positive charge on nitrogen site N_3 (see Fig. 5) and carbon site 1 as virtually unscreened; the interaction with sites 2 and 3 as half screened and sites beyond this as completely screened. Our choice is based on the picture that the migration of negative charge from the vicinity of C_2 and C_3 towards C_1 would partially screen the field produced by the

positive charge on N_3 so that at C_4 the interaction would be effectively reduced to zero. We arrive at the figure of $\frac{1}{2}$ for the screening of sites 2 and 3 because half of the atomic orbital adjacent to the nitrogen site on these sites is practically unscreened, while the opposite side is quite strongly screened. There is very little material between the nitrogen site and each of these three carbon sites, so that it seems reasonable to leave the Coulomb interaction with the dielectric constant that of free space. In Table I we tabulate the distances between the nitrogen site and each carbon site. We include also the matrix element for each site, j, in Eq. (4.5) computed for $Q=0$ and $Q=\pi/a$ using the approximate form of the α's and β's given after Eq. (4.1) and (4.5) and the unmodified Coulomb interaction limited in the manner described above.

It is reasonable to neglect the interaction with the positive charge on the remote nitrogen site on the ψ_- structure because the distance to the spine is about 14 Å and the interaction is further reduced by the dielectric constant of the material of the side chain. This dielectric constant must be similar to that of benzene which is about 2.2. This gives a total matrix element of 0.1 eV for $Q=0$ which we can neglect compared to the total computed in Table I considering the approximations we have made.

In order to calculate the side-chain induced electron-electron interaction, we must know the energy $\hbar\omega$ for the transitions of the side chains. For an isolated side-chain molecule of 1,1'-diethyl-4,4'-cyanine iodide the absorption maximum for the transition we are considering occurs at 600 mμ giving a value of 2 eV for $\hbar\omega$.[7]

In the polymer the side chains will interact with one another and change the frequency of oscillation to some extent, but as the molecules are quite well separated and the charges are quite well screened from one another, let us take the frequency to be about 2 eV nevertheless. Then the side-chain induced attraction $V \approx \langle 2V(Q)^2 \rangle_{av}/G\hbar\omega$ will be approximately -3.5 eV/G where we have taken the mean of the square of the interaction for $Q=0$ and $Q=\pi/a$ as given in Table I. This is greater than the Coulomb repulsion of 1.5 eV/G estimated in (4.4) so that the net interaction is an attractive one,

$$V \approx -2 \text{ eV}/G. \qquad (4.7)$$

The reason this is so strongly attractive is that we have seen to it that the nitrogen sites lie close to the spine so that the matrix element (4.6) is large and at the same time have chosen a side chain with a fairly low-frequency transition so that $\hbar\omega$ is small.

Some idea of the superconducting transition temperature now can be obtained by estimating the density of states for the electrons in the spine, $N(0)$. This can be done in the following way. The spine itself is very similar to a conjugated polyene chain $\{CH=CH-\}_n$ except that the side chains replace certain of the hydrogens so that one can crudely estimate the density

TABLE I. Carbon-nitrogen distances and matrix elements.

Carbon site	Distance to N_3 (Å)	Matrix element $V(Q)$ (eV)	
		$Q=0$	$Q=\pi/a$
1	1.5	0.76	0.41
2	2.5	0.47	0.11
3	3.0	0.47	0.11
4	(4.5)	0.76	0.41
		Total 2.46	1.04

of states in the spine from a knowledge of it in a polyene chain. The benzene ring is essentially a triene {CH=CH—} tied back on itself in the form of a loop and can be described in terms of a simple band picture.[9],[10] The first absorption at 250 mμ is believed to correspond to a transition of a π-electron from a $m=1$ to $m=2$ state which is approximately half the total width of the band. The total width of the band for benzene is thus ≈ 10 eV and should be approximately the same for the polyene chain. If we assume the ϵ versus k curve is parabolic up to the halfway point in the band (up to 5 eV), then the density of states of one spin at the Fermi surface is approximately $\frac{1}{8}G$ states/eV. This is probably a reasonable estimate of the density of states as it corresponds to an effective mass for the electrons in the spine of 0.7 the electron mass.

If there was no bond localization in the spine, then we could use Eq. (2.9) to estimate the superconducting transition temperature using (4.3) and the above density of states. One obtains a temperature ≈ 2200°K in this case! This extremely high transition temperature can be understood when it is realized that in the chosen structure it is an electronic oscillation which provides the coupling between the electrons rather than the oscillation of the nuclei as in a conventional superconductor. The simple argument of the isotope effect that the transition temperature for a phonon-coupled superconductor is proportional to $1/M^{1/2}$, where M is the isotopic mass of the nuclei indicates that for an electron-coupled superconductor the transition temperature should be a factor of $(M/m)^{1/2}$ (i.e., ≈ 300) times larger. This is, perhaps, too glib an answer for it is necessary to choose the over-all structure so as to obtain a sufficiently strong coupling matrix element (2.6). Our particular model illustrates this in detail.

If there is considerable bond localization in the spine, then our inequality (3.4) shows that the superconducting state can still occur if the semiconductor gap δ is somewhat less than 0.67 eV. If this is satisfied, the transition temperature in this case should still be several hundred °K.

For transition temperatures as high as this the coherence energy of the superconducting state becomes comparable to the chemical binding energy. This energy is approximately

$$W_0 = -2N(0)(\hbar\omega)^2 \exp[-2/(N(0)|V|)]. \quad (4.8)$$

In our example, the coherence energy is about 0.1 eV per unit cell of the chain. This is not very large, however, if one synthesized a polymer in which the density of states is large but $|V|$ is small so as to obtain the same transition temperature, then the coherence energy would become quite large. A coherence energy of as much as 1 eV per unit cell of the chain appears possible

in such a polymer. As this energy is comparable to the resonance energy of the benzene ring, one should expect a considerable stabilization of the polymer on this account. It is interesting to note, too, that the destruction of superconductivity at one point in the chain raises the energy by the coherence energy per unit length times the coherence length ζ_0. The coherence length ζ_0 for these molecules should be about 30 Å as it is inversely proportional to T_c and $\zeta_0 \approx 10^4$ Å for conventional superconductors. Consequently, it would require a large amount of energy to destroy the superconductivity locally.

V. DISCUSSION

We believe that while the estimates for the various matrix elements in the above example are crude, they are not unrealistic. This forces upon us the remarkable conclusion that superconductivity could and should occur in structures such as this even at room temperatures. There are many other possible structures similar to the one shown involving a semiconducting chain for the spine and a dye-like molecule for the side chain which would also be superconducting. It is unlikely that our particular choice described above would be the easiest to synthesize or have the optimum superconducting properties, but it illustrates the possibility in a detailed manner.

In these molecules we should expect the usual electrical properties of a metallic superconductor, however, in order to observe such effects contact would have to be made to the ends of the spine. This could be a difficult problem to solve, but may be possible by cross-linking the spines so as to form a three-dimensional net of the filamentary molecules. Because of the large transition temperature, one would expect the critical field for the destruction of superconductivity to be very high compared to that of conventional superconductors. The highly divided filamentary structure of a bulk sample of the polymer should mask any appreciable Meissner effect. Perhaps the most interesting feature of these molecules, however, lies in the phase correlation of the electron pairs throughout the molecule. This phase correlation should impose certain restraints upon the ability of the molecule to react chemically with other such molecules. The reason is that in order to form a covalent bond, the electrons must interfere constructively in the region of positive potential. Consequently, the relative phase of the electrons forming the bond are important. Such an effect has been discussed briefly by Ambegaokar and Baratoff[11] in regard to tunneling between conventional superconductors in the Josephson effect. The superconducting state is unique in that this long-range phase correlation, "off-diagonal-long-range-order" (ODLRO)[6] distinguishes it from the normal or insulating states. This we have shown can occur even

[9] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), p. 234.
[10] C. R. Noller, *Chemistry of Organic Compounds* (W. B. Saunders Co., Philadelphia, 1960), 2nd ed., p. 665.

[11] V. Ambegaokar and A. Baratoff, Phys. Rev. Letters **10**, 486 (1963).

in our structure which is essentially a one-dimensional chain, which is in striking contrast to a classical one-dimensional interacting chain such as the Ising chain which cannot exhibit long-range order.[12] Because of this ODLRO, which is a property of the molecule as a whole and the above chemical properties which are related to it, these molecules will have the property of reacting as a single entity which is precisely what London[1] was seeking to understand in regard to biologically important macromolecules.

In regard to the possible biological significance of our results, it is appropriate to mention a theorem which was established by Wigner[13] on the probability of a quantum mechanical system reproducing itself. He succeeded in showing that under two reasonable assumptions, this probability is essentially zero. The relevant assumption is that his "collision matrix" S, which generates the final state from the initial state, is assumed to be a random matrix. This assumption may be violated in the superconducting state because of the singular nature of the pair distribution associated with ODLRO. It would be useful to reexamine Wigner's theorem to see whether a *superconducting* quantum system would be capable of reproducing. The curious chemical selectivity mentioned earlier suggests that this may be the case.

ACKNOWLEDGMENTS

Note added in proof. It is appropriate to clarify a point in regard to the band structure of our chosen model. The partial charges on the nitrogen sites of the side chains produce a periodically varying potential along the spine with a fundamental period of $4a$. This produces a gap at $k = \pi/4a$ but no gap at $\pi/2a$ where the Fermi surface lies. The reason there is no gap at $\pi/2a$ is that in the tight binding approximation, where one can consider an electron as sampling the potential at all points within a particular orbital before moving on, the effective potential of each orbital may be taken as that of the appropriate carbon nucleus. From a calculation similar to that of Table II, one can easily show that there is then no Fourier component of period $2a$ and therefore no gap at the Fermi surface. The only effect which tends to produce a semiconductor gap (i.e., one at the Fermi surface) is the tendency for the double bond to localize at alternate sites. This was considered in Sec. III, where we showed that for a fixed semiconductor gap, the superconducting state should occur if a particular inequality could be satisfied. The band gap produced by bond alternation, however, is not fixed, but depends upon the amplitude of the periodic distortion; consequently, the actual gap and distortion must be determined in a self-consistent manner. In this case our earlier arguments do not apply and whether the superconducting state or the semiconductor state occurs depends upon which has the lower energy. Longuet-Higgins and Salem [Proc. Roy. Soc. (London) **A251**, 172 (1959)] have calculated the stabilization energy for a polyene with alternation of bond lengths and obtain an energy of 0.019 kcal/mole per bond (≈ 0.001 eV/bond) for the semiconductor state. We have calculated it for the superconducting state [Eq. (4.8)] and obtain (≈ 0.025 eV/bond) so that, in our model, the superconducting state should be favored.

Finally, our calculation has shown that a phase transition from the normal to the superconducting state should occur even in our one-dimensional system. This is unusual [see, for example, L. van Hove, Physica **16**, 137 (1950)] and one may question whether our result follows because the BCS theory, upon which it is based, is not sufficiently exact. We have some reason for believing that our conclusions are valid nevertheless, but this point requires further investigation.

[12] J. Ashkin and W. E. Lamb, Jr., Phys. Rev. **64**, 159 (1943).
[13] E. P. Wigner, in *The Logic of Personal Knowledge* (Polanyi Festschrift) (Routledge and Kegan Paul, London, 1961), p. 231.