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Possibility of Superconductive-Type Enhanced Conductivity in DNA at Room Temperature

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Applying Little's formalism to investigate the possibility of superconductive regions at room temperature in organic polymers, we have calculated the Coulomb and effective attractive terms for the polycytosine homopolynucleotide. Little's original idea that the effective interaction between the mobile electrons of the spine is due to the polarization of the side-chain electrons has been extended to take into account the polarization of the σ electrons of the same systems which provide the mobile electrons. According to the results obtained for many intraband and interband scattering processes, the absolute value of the attractive term is larger than, or about the same as, that of the Coulomb term. Therefore, we cannot exclude the possibility of superconductive-type enhanced conductivity in some regions of DNA. Finally, the effects of the finite dimensions of a cytosine molecule are discussed from the point of view of screening and thermodynamic fluctuations.

I. INTRODUCTION

In 1964, Little[1] raised the interesting idea that if we have a one-dimensional organic polymer containing a delocalized electron system in the main chain and a localized one in the side chains, the effective attraction between the electrons of the delocalized system due to the polarization (virtual excitations) of the electrons in the side chains may result in a superconductive state for the delocalized electrons. In this essentially BCS-type theory,[2] the excitation of the side-chain electrons plays the role of the phonons. Since the electron mass is ~1/2000 of the proton mass, he estimated the transition temperature of an organic model polymer to be ~2200°K.

This hypothesis of Little's has raised considerable discussion. Ferrell[3] has pointed out that in an infinite one-dimensional system the possibility of superconductivity is ruled out because thermodynamic fluctuations will make off-diagonal long-range order (ODLRO). DeWames *et al.*,[4] on the other hand, have shown that this is not the case if the polymer is long but not infinite. Later, Rice[5] has pointed out that ODLRO is inconsistent with Yang's criterion for one-, and two-dimensional systems. Kuper[6] and Paulus[7] have pointed out that the Coulomb interaction cannot be screened in a polyene with side chains, and therefore the attractive interaction will be smaller than the repulsive one, ruling out the possibility of superconductivity.

Little, in a later paper,[8] analyzed in detail the effect of fluctuations on the possibility of superconductivity. He came to the conclusion that though in a one-dimensional system a true superconductive state with a sharp transition temperature cannot exist, the possibility remains of having greatly enhanced conductivity in some local regions of a polymer, which decreases only gradually in a critical temperature region. Further, he pointed out that if the polymer has finite size in the two other directions and is interacting with its environment, the effect of thermodynamic fluctuations will be smaller.

In a previous note[9] we have shown that Little's original formalism does not require side chains, but we can use the polarization of the σ electrons of a main chain which has delocalized π electrons to obtain the effective attractive interaction. In our paper we applied this idea for the polyene and "polyethylene" systems. Here we made an error, as Paulus[7] has pointed out, in the case of the C-C bond of polyene, giving the value of -6.6 eV for its contribution to the attractive term instead of zero. On the other hand, our estimate of the attractive contribution of a C-H bond of -3.5 eV for polyene and of -7.2 eV for "polyethylene" is correct, and therefore Paulus's conclusion that the polarization of electrons will give only an unimportant contribution is in our opinion, unjustified. The corrected V_1+V_2 values (for notation see Ref. 9) for polyene and "polyethylene" are thus $17.7-3.5=14.2$ eV and $21.5-7.2=14.3$ eV, respectively.

We see, however, another reason for objecting to the role of the polarization of the σ electrons in the attractive term. Namely, according to recent *ab initio* calculations[10] on unsaturated organic molecules, the condition of σ-π separability are not fulfilled. We shall return to this point somewhat later.

Little[1] has suggested already in his original paper that room-temperature superconductivity may exist in DNA and may play a biological role. Very recently Pearlstein[10] has also considered this subject. Because we had at our disposal band structures for different periodic DNA models,[11] as a first step in investigating

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[1] W. A. Little, Phys. Rev. **134A**, 1416 (1964).
[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[3] R. A. Ferrell, Phys. Rev. Letters **13**, 330 (1964).
[4] R. E. DeWames, G. W. Lehman, and T. Wolfram, Phys. Rev. Letters **13**, 749 (1964).
[5] T. M. Rice, Phys. Rev. **140**, A1889 (1965).
[6] C. G. Kuper, Phys. Rev. **150**, 189 (1966).
[7] K. F. G. Paulus, Mol. Phys. **10**, 381 (1965).
[8] W. A. Little, Phys. Rev. **156**, 396 (1967).
[9] J. Ladik, G. Biczó, and A. Zawadowski, Phys. Letters **18**, 257 (1965).
[10] R. M. Pearlstein, Phys. Rev. Letters **20**, 594 (1968).
[11] J. Ladik and K. Appel, J. Chem. Phys. **40**, 2470 (1964).

the possibility of superconductive-type enhanced conductivity in DNA at room temperature, we have calculated the repulsive Coulomb term and the effective attractive term for the polycytosine ($\mathcal{C}\mathcal{C}\mathcal{C}\mathcal{C}\cdots$) periodic DNA model using Little's formalism. In this system only the π orbitals of the superimposed cytosine ($\mathcal{C}$) molecules are interacting to a non-negligible extent, and therefore we can take only the π electrons as delocalized ones and the σ electrons as localized to a given nucleotide base. Further, as is well known, the π-π^* and σ-σ^* excitations have very different energies. Therefore, we can assume that the π electrons can be considered approximately from the point of view of Little's mechanism as a separate electronic system from the σ-electron system, and thus, though the σ-π separability is not rigorously fulfilled in these molecules, the σ electrons can play the role of the side chains of Little's original polymer.

In the calculation we have assumed only first-neighbor interactions, and for these interactions we have not introduced screening. By this approximation we have certainly underestimated the magnitude of the Coulomb term with respect to the attractive term to a smaller extent than Little[1] did, because the distance of two neighboring cytosine molecules, is $\sim$3.4 Å.

Since the Fermi level of poly-$\mathcal{C}$ is in the forbidden band between the valence and conduction bands, and therefore the estimation of the density of states at the Fermi level [$N(0)$] seems to be problematic, we have not tried to calculate the transition temperature T_c. The aim of the present paper was only to calculate the Coulomb and attractive terms for the different bands of poly-$\mathcal{C}$ using the same approximations for both terms (see Sec. II). By this means we wanted to investigate whether DNA satisfies the necessary (but of course not sufficient) condition for superconductivity, that in some cases the absolute value of the attractive term must be larger than the repulsive one; if this condition is not satisfied, the possibility of enhanced conductivity in some regions of DNA must be ruled out completely.

II. METHOD

Generalizing Little's expression[1] (2.1) to the case where we have many atoms in the elementary cell, we can write the one-electron LCAO (linear combination of atomic orbitals) crystal orbital of a π electron of the spine in the form

$$\phi_{k,m}(\mathbf{r})=G^{-1/2}\sum_{i=1}^{G}\sum_{l=1}^{g}e^{ikR_i}c_{m,l}(k)\phi_l(\mathbf{r}-\mathbf{R}_{i,l})\,, \qquad (1)$$

where G is the number of the elementary cells, g is the number of π orbitals in one elementary cell, k is the wave number, m is the band index, and $\phi_l(\mathbf{r}-\mathbf{R}_{i,l})$ is a π AO centered on the lth atom in the ith elementary cell. Furthermore, $\mathbf{R}_{i,l}=\mathbf{R}_i+A_i\mathbf{R}_{1,l}$ is the position vector of the lth atom in the ith elementary cell, R_i is the absolute value of $\mathbf{R}_i=(i-1)\mathbf{a}$, A_i is a matrix of order three representing the rotation of the ith elementary cell with respect to the first one around the axis of the helix, and finally $\mathbf{a}$ is the lattice vector. The coefficients $c_{m,l}(k)$ have been determined with the aid of a LCAO crystal-orbital calculation on poly-$\mathcal{C}$.[11]

As mentioned in the Introduction, we have taken into account, instead of the side chains, the virtual excitations of the σ electrons of the same nucleotide bases which provide the delocalized π-electron system.[12] For the many-electron wave function of the σ electrons we can write formally

$$X_{q,n}(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_{2h})=G^{-1/2}\sum_{j=1}^{G}e^{iqR_j}\Psi_n(\mathbf{r}_1-\mathbf{R}_j,\ \mathbf{r}_2-\mathbf{R}_j,\cdots,\mathbf{r}_{2h}-\mathbf{R}_j) \qquad (2)$$

[see Eq. (2.2) of Ref. 1], where q is the wave number of the σ electrons and $2h$ is the number of σ electrons in one cytosine molecule. Ψ_0 ($n=0$) means the Slater determinant of the closed-shell ground state, and if n is not zero we have the singlet excited state

$$\begin{aligned}\Psi_n(1,2,\cdots,2h)=[2(2h)!]^{-1/2}&\\ \times\{\det[\psi_1(1)\alpha(1),\cdots&\\ \times\psi_n(2n-1)\alpha(2n-1),\bar{\psi}_n(2n)\beta(2n),\cdots]&\\ -\det[\psi_1(1)\alpha(1),\cdots,\psi_n(2n-1)\beta(2n-1),&\\ \bar{\psi}_n(2n)\alpha(2n),\cdots]\}\,,&\qquad (3)\end{aligned}$$

which arises from the excitation of an electron from the nth bonding MO to the corresponding antibonding one. Because σ electrons are mostly localized on two centers, we can approximate the σ MO's in the two-center LCAO form

$$\psi_n(1)=d_{n,r}\chi_r(1)+d_{n,s}\chi_s(1)\,, \qquad (4)$$

where χ_r and χ_s are those two AO's to which a given σ electron is localized. We will denote the corresponding two-center antibonding orbital by a bar above the letter d.

The Coulomb repulsion term between two electrons of the delocalized system is

$$\begin{aligned}C(k_1,m_1,k_2,m_2,k_1',m_1',k_2',m_2')&\\ =G\int\int\phi_{k_1',m_1'}{}^*(\mathbf{r}_1)\phi_{k_2',m_2'}{}^*(\mathbf{r}_2)r_{12}{}^{-1}\phi_{k_1,m_1}(\mathbf{r}_1)&\\ \times\phi_{k_2,m_2}(\mathbf{r}_2)dv_1dv_2\,,&\qquad (5)\end{aligned}$$

where k_1 and m_1 are the wave number and the band index of electron 1 before the scattering, and k_2 and m_2 are the same quantities for electron 2. The primed indices mean the corresponding quantities after the

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[12] In a polynucleotide such as poly-$\mathcal{C}$ we have, of course, the sugar-phosphate groups as side chains. Of course, the effect of these could be taken into account also, but we have neglected them in the present calculation, underestimating in this way the absolute value of the attractive term.

scattering process. Substituting (1) into (5), taking into account only nearest-neighbor interactions, and neglecting differential overlap, we obtain, after a somewhat lengthy but simple calculation,

$$C(k_1,m_1,k_2,m_2,k_1',m_1',k_2',m_2')$$
$$=2\sum_{l,t=1}^{g} c_{m_1,l}(k_1)c_{m_2,t}(k_2)c_{m_1',l}(k_1')^* \times c_{m_2',t}(k_2')^* C_{l,t}, \quad (6)$$

where[13]

$$C_{l,t}=B_{l,t}^{(6)}+D_{l,t}e^{i\pi(k_1'-k_1)}+D_{t,l}e^{-i\pi(k_1'-k_1)}, \quad (7a)$$

$$D_{l,t}=(1-A_{l,t})^2F_{l,t}^{(6)}+2A_{l,t}(1-A_{l,t}) \times[F_{l,t}^{(1)}-2F_{l,t}^{(8)}]+A_{l,t}^2F_{l,t}^{(7)}, \quad (7b)$$

$$F_{l,t}^{(1)}=C_{\pi\sigma\pi\sigma}(R_{l,t}^+), \quad F_{l,t}^{(6)}=C_{\pi\pi\pi\pi}(R_{l,t}^+), \quad (7c)$$

$$F_{l,t}^{(7)}=C_{\sigma\sigma\sigma\sigma}(R_{l,t}^+), \quad F_{l,t}^{(8)}=C_{\pi\pi\sigma\sigma}(R_{l,t}^+), \quad (7d)$$

and finally

$$B_{l,t}^{(6)}=C_{\pi\pi\pi\pi}(R_{l,t}). \quad (7e)$$

The two-center Coulomb integrals $C_{\pi\sigma\pi\sigma}$, etc., occurring in these expressions are defined in Preuss's tabulation,[14] $R_{l,t}$ stands for the distance between atomic nuclei l and t in the same cell, and $R_{l,t}^+$ stands for the same quantity if center l is in one cell and t in the nearest neighboring cell. Finally, $A_{l,t}=\cos^2\vartheta_{l,t}$, where the angle $\vartheta_{l,t}$ is defined in Fig. 1.

Little has given the following expression for the matrix element of the effective attractive interaction [Eq. (2.3) of Ref. 1]:

$$V(k_i,m_i,q,0,k_i',m_i',q',n)$$
$$=G\int\cdots\int \phi_{k_i',m_i'}^*(\mathbf{r})X_{q',n}^*(\mathbf{r}_1,\cdots,\mathbf{r}_{2h}) \times\Big(\sum_{s=1}^{2h}|\mathbf{r}-\mathbf{r}_s|^{-1}\Big)\phi_{k_i,m_i}(\mathbf{r})X_{q,0}(\mathbf{r}_1,\cdots,\mathbf{r}_{2h}) \times dv\,dv_1\cdots dv_{2h}, \quad (i=1,2). \quad (8)$$

Substituting (1), (2), (3), and (4) with $n=0$ for Ψ_n (ground state) into (8), introducing the notation[15]

$$V(k,m,k',m',n)=V(k,m,q,0,k',m',q',n),$$

again taking into account only nearest-neighbor interactions, and neglecting differential overlap, we obtain

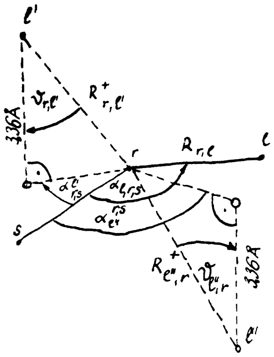

FIG. 2. Definition of angles $\alpha_{l,r,s}$, $\alpha_{r,s}{}^{l}$, and $\alpha_l{}^{r,s}$. The atoms r, s, and l are in the plane of the same $\mathcal{C}$ molecule. Atoms l' and l'' are in the planes of the nearest-neighbor molecules in opposite directions. $\alpha_{r,s}{}^{l'}$ is the angle between the straight line rs and the projection of the line rl onto the plane defined by the points r, s, and l. The angle $\alpha_{l''}{}^{r,s}$ is defined in a similar way, for atom l''.

after a somewhat lengthy but simple calculation:

$$V(k_i,m_i,k_i',m_i',n)=2\sqrt{2}\sum_{l=1}^{g} c_{m_i,l}(k_i)c_{m_i',l}(k_i')^+ \times[d_{n,r}\bar{d}_{n,s}V_{r,s}{}^{l}+d_{n,s}\bar{d}_{n,r}V_{s,r}{}^{l}], \quad (i=1,2) \quad (9)$$

where

$$V_{r,s}{}^{l}=J_{l,r,s}+J_{r,s}{}^{l}e^{-i\pi(k_i'-k_i)}+J_l{}^{r,s}e^{i\pi(k_i'-k_i)}, \quad (10a)$$

$$J_{l,r,s}=\tfrac{1}{3}(2\cos^2\alpha_{l,r,s}B_{l,r}^{(1)}+2\sin^2\alpha_{l,r,s}B_{l,r}^{(2)} +2\sqrt{2}\cos\alpha_{l,r,s}B_{l,r}^{(3)}+B_{l,r}^{(4)}), \quad \text{for}\quad r=1,2,\cdots,g, \quad (10b)$$

$$J_{l,r,s}=B_{l,r}^{(5)}, \quad \text{for}\quad r=g+1,\ g+2,\ \cdots,\ g+f. \quad (10c)$$

Here f is the number of atoms which do not have a π orbital, and

$$B_{r,l}^{(1)}=C_{\pi\sigma\pi\sigma}(R_{r,l}), \quad B_{r,l}^{(2)}=C_{\pi\pi'\pi\pi'}(R_{r,l}),$$
$$B_{r,l}^{(3)}=C_{\pi\sigma\pi s}(R_{r,l}), \quad B_{r,l}^{(4)}=C_{\pi s\pi s}(R_{r,l}), \quad (10d)$$
$$B_{r,l}^{(5)}=C_{\pi k\pi k}(R_{r,l}).$$

Further,

$$J_{r,s}{}^{l}=\tfrac{1}{3}\{2[A_{r,l}+\cos^2\alpha_{r,s}{}^{l}(1-A_{r,l})(1-2A_{r,}{}^{l})F_{r,l}^{(1)}] +A_{r,l}[F_{r,l}^{(5)}+2\cos^2\alpha_{r,s}{}^{l}(1-A_{r,l}) \times(F_{r,l}^{(6)}+F_{r,l}^{(7)}+F_{r,l}^{(8)})]+(1-A_{r,l}) \times(F_{r,l}^{(4)}+2\sin^2\alpha_{r,s}{}^{l}F_{r,l}^{(2)})+2\sqrt{2}\cos\alpha_{r,s}{}^{l} \times(1-A_{r,l})^{1/2}[A_{r,l}(F_{r,l}^{(9)}+2F_{r,l}^{(10)}) +(1-A_{r,l})F_{r,l}^{(3)}]\}, \quad \text{for } r=1,2,\cdots,g \quad (11a)$$

$$J_{r,s}{}^{l}=A_{r,l}F_{r,l}^{(11)}+(1-A_{r,l})F_{r,l}^{(12)}, \quad \text{for}\quad r=g+1,g+2,\cdots,g+f, \quad (11b)$$

where the quantities $F_{r,l}^{(1)}$, $F_{r,l}^{(6)}$, $F_{r,l}^{(7)}$, $F_{r,l}^{(8)}$ have been defined previously [see Eqs. (7c) and (7d)], $A_{r,l}$ was defined in Fig. 1,

$$\left.\begin{array}{ll} F_{r,l}^{(2)}=C_{\pi\pi'\pi\pi'}(R_{r,l}^+), & F_{r,l}^{(3)}=C_{\pi\sigma\pi s}(R_{r,l}^+), \\ F_{r,l}^{(4)}=C_{\pi s\pi s}(R_{r,l}^+), & F_{r,l}^{(5)}=C_{\sigma s\sigma s}(R_{r,l}^+), \\ F_{r,l}^{(9)}=C_{\sigma\sigma\sigma s}(R_{r,l}^+), & F_{r,l}^{(10)}=C_{\pi\pi\sigma s}(R_{r,l}^+), \\ F_{r,l}^{(11)}=C_{\sigma k\sigma k}(R_{r,l}^+), & F_{r,l}^{(12)}=C_{\pi k\pi k}(R_{r,l}^+). \end{array}\right\} \quad (11c)$$

(The notation for the integrals, may again be found

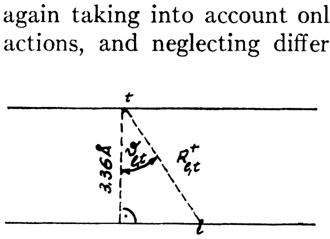

FIG. 1. Definition of the angle $\vartheta_{l,t}$. The two solid lines indicate two superimposed cytosine molecules.

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[13] By the conservation of momentum $\mathbf{k}_1+\mathbf{k}_2=\mathbf{k}_1'+\mathbf{k}_2'$, therefore, we can express the difference $\mathbf{k}_2-\mathbf{k}_2'$ occurring in our expression as $\mathbf{k}_1'-\mathbf{k}_1$.

[14] H. Preuss, *Integraltafeln für Quantenchemie, Band I.* (Springer-Verlag, Berlin-Göttingen-Heidelberg, 1956), p. 7.

TABLE I. Typical values of some Coulomb integrals occurring in the calculation (in eV).[a]

		$R_{l,t}$	$R_{l,t}^+$	$C_{\pi\pi\pi\pi}(R)$		$C_{\pi\sigma\pi\sigma}(R)$		$C_{\pi k\pi k}(R)$	
l	t	(Å)		$R=R_{l,t}$	$R=R_{l,t}^+$	$R=R_{l,t}$	$R=R_{l,t}^+$	$R=R_{l,t}$	$R=R_{l,t}^+$
1 (N)	1 (N)	0	3.67	19.81	7.30	17.68	7.49	···	···
2 (C)	2 (C)	0	3.94	16.29	6.76	14.54	6.95	···	···
7 (O)	7 (O)	0	3.96	23.22	6.27	20.72	6.95	···	···
1 (N)	2 (C)	1.36	3.58	9.34	3.93	10.39	4.06	···	···
2 (C)	7 (O)	1.23	3.47	10.31	4.06	11.46	4.16	···	···
4 (C)	5 (C)	1.40	5.41	8.90	2.64	11.34	2.68	···	···
3 (N)	9 (H)	1.00	4.25	···	···	···	···	11.87	3.37
4 (C)	10 (H)	1.10	5.02	···	···	···	···	10.71	2.83

[a] See the text between Eqs. (7c) and (11c) for the details of the notation. The method of calculation and the parameter values are given in the text after Eq. (13). The numbering of the atoms within the elementary cell is given in Fig. 3.

in Ref. 14.) We can immediately obtain the expression for $J_1^{r,s}$ from (11a) and (11b) if instead of $A_{r,l}$ we substitute $A_{l,r}$, change all the quantities $F_{r,l}^{(p)}$ ($p=1, \cdots, 12$) to $F_{l,r}^{(p)}$, and finally all the angles $\alpha_{r,s}{}^l$ to $\alpha_l{}^{r,s}$. The definition of the angle $\alpha_{l,r,s}$, $\alpha_{r,s}{}^l$, and $\alpha_l{}^{r,s}$ is given in Fig. 2.

Following Little [see the text after Eq. (2.6) of Ref. 1], we can write the effective attractive term which arises in consequence of all σ electrons of the cytosine molecule in the form

$$A(k_i,m_i,k_i',m_i') = -K\sum_n |V(k_i,m_i,k_i',m_i',n)|^2\lambda_n, \qquad (i=1,\,2) \quad (12)$$

where λ_n is the wavelength of the $\sigma \longrightarrow \sigma^*$ excitation of the nth σ bond (in mμ) and the constant $K=0.5973$ if we want to obtain A in eV.†

Note added in proof. Since, as the vacuum ultraviolet spectrum of a complicated saturated molecule shows it, the σ electrons in the different σ bonds of it can be excited independently from each other (the σ electrons do not form a common delocalized σ system, at least from the point of view of excitations), we can assume the simultaneous polarization of all the σ bands in a cytosine molecule. Therefore to calculate A we had to sum their contributions in Eq. (12).

The total energy of interaction per unit cell (cytosine molecule) will then be[16]

$$\begin{aligned}\Delta(k_1,m_1,k_2,m_2,\,k_1',m_1',k_2',m_2') &= -\tfrac{1}{2}[A(k_1,m_1,k_1',m_1') \\ &\quad + A(k_2,m_2,k_2',m_2')] + C(k_1,m_1,k_2,m_2,k_1',m_1',k_2',m_2') \\ &= -\tfrac{1}{2}(A_1+A_2)+C=\tilde{A}+C. \quad (13)\end{aligned}$$

We have substituted the eigenvector components $c_{m_i,l}(k_i)$, obtained from the previously mentioned LCAO crystal-orbital calculation of the band structure of poly-C,[11] into (6) and (9). All the integrals occurring in (6) and (9) have been calculated using the known geometry of DNA *B*.[17] The same geometry has been used for the determination of the angles $\alpha_{l,r,s}$, $\alpha_{r,s}{}^l$, and $\alpha_l{}^{r,s}$. The different integrals (7c), (7a), (7e), (10a), and (11c) have been calculated with the aid of expressions and integral tables due to Roothaan,[18] Preuss,[14] Kotani *et al.*,[19] and Ishiguro *et al.*,[20] using for the effective nuclear charges the values given by Burns[21] for 2*s* and 2*p* electrons (for C, $\frac{1}{2}Z_{\text{eff}}=1.53$; for N, $\frac{1}{2}Z_{\text{eff}}=1.86$; and for O, $\frac{1}{2}Z_{\text{eff}}=2.18$). The heteroatomic two-center integrals that occur have been approximated as homocentric two-center integrals, for which the value $\frac{1}{2}(Z_{\text{eff}}{}^{(r)}+Z_{\text{eff}}{}^{(s)})$ has been used. For comparison, we give in Table I some typical values of the Coulomb integrals that occur. The numbering of the atoms within the elementary cell containing one cytosine molecule is given in Fig. 3. The coefficients of the two-center bonding and antibonding LCAO MO's occurring in (9) have been determined with the aid of Del Re's method.[22] The wavelengths of the $\sigma \longrightarrow \sigma^+$ excitation energies were taken from the Rao's book.[23] We have used for the C-H bonds $\lambda=125$ mμ, for the N-H bonds $\lambda=152$ mμ, for the C-C bonds $\lambda=135$ mμ, for the C-N

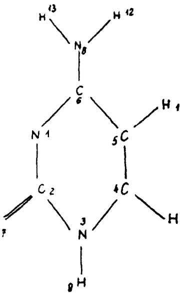

FIG. 3. Numbering of the atoms within the elementary cell containing one cytosine molecule.

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[15] Here we have used again the relation $\mathbf{k}'-\mathbf{k}=\mathbf{q}-\mathbf{q}'$, which is the consequence of the conservation of momentum.

[16] We have not averaged our expressions over k_i and k_i' ($i=1,2$), but following Little, we have performed all the calculation for values k_i and k_i', respectively, corresponding to the limits of the bands.

[17] R. Langridge, B. A. Marwin, W. E. Seeds, H. R. Wilson, C. W. Hooper, M. H. F. Wilkins, and L. D. Hamilton, J. Mol. Biol. **2**, 38 (1960).

[18] C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).

[19] M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen Co., Ltd., Tokyo, 1955).

[20] E. Ishiguro, T. Arai, M. Sakamoto, and T. Takayanagi, Nat. Sci. Rept. Ochanomizu Univ. **5**, 157 (1955).

[21] G. Burns, J. Chem. Phys. **41**, 1521 (1964).

[22] G. Del Re, J. Chem. Soc. 4031 (1958); G. Del Re, Nuovo Cimento **17**, 644 (1960).

[23] C. N. Rao, *Ultra-Violet and Visible Spectroscopy* (Chemical Applications, London, Butterworths, 1961).

TABLE II. The values of the Coulomb term (C), of the average attractive term (A), and their sum (Δ) in eV per cell (see Ref. 24).

ak_1	m_1[a]	ak_2	m_2[b]	ak_1'	m_1'[c]	ak_2'	m_2'[d]	C	A_1[e]	A_2[f]	$\tilde{A}$	Δ
0	4	0	4	0	4	0	4	18.75	−21.79	−21.79	−21.79	−3.04
π	4	π	4	π	4	π	4	19.01	−22.83	−22.83	−22.83	−3.82
0	4	π	4	0	4	π	4	18.86	−21.79	−22.83	−22.31	−3.45
0	4	π	4	π	4	0	4	4.22	− 4.69	− 4.69	− 4.69	− 0.47
0	5	0	5	0	5	0	5	15.25	−15.28	−15.28	−15.28	−0.03
π	5	π	5	π	5	π	5	14.98	−13.92	−13.92	−13.92	1.06
0	5	π	5	0	5	π	5	15.06	−15.28	−13.92	−14.60	0.46
0	5	π	5	π	5	0	5	2.0	− 1.56	− 1.56	− 1.56	0.44
0	6	0	6	0	6	0	6	15.66	−13.56	−13.56	−13.56	2.10
π	6	π	6	π	6	π	6	15.74	−13.60	−13.60	−13.60	2.14
0	6	π	6	0	6	π	6	15.70	−13.56	−13.60	−13.58	2.12
0	6	π	6	π	6	0	6	2.59	− 1.67	− 1.67	− 1.67	0.92
Interband scattering processes												
0	4	0	5	0	4	0	5	13.25	−21.79	−15.28	−18.54	−5.29
π	4	π	5	π	4	π	5	13.41	−22.83	−13.92	−18.38	−4.97
0	4	π	5	0	4	π	5	13.41	−21.79	−13.92	−17.86	−4.45
0	4	0	5	0	5	0	4	1.48	− 1.82	− 1.82	− 1.82	−0.34
π	4	π	5	π	5	π	4	1.60	− 1.81	− 1.81	− 1.81	−0.21
0	4	π	5	π	5	0	4	1.38	− 1.53	−1.53	− 1.53	−0.15
0	4	0	6	0	4	0	6	14.02	−21.79	−13.56	−17.68	−3.66
π	4	π	6	π	4	π	6	14.14	−22.83	−13.60	−18.22	−4.08
0	4	π	6	0	4	π	6	14.05	−21.79	−13.60	−17.70	−3.65
0	4	0	6	0	6	0	4	1.36	− 1.36	− 1.36	− 1.36	0.00
π	4	π	6	π	6	π	4	1.37	− 1.36	− 1.36	− 1.36	0.01
0	4	π	6	π	6	0	4	1.20	− 1.26	− 1.26	− 1.26	−0.06
0	5	0	6	0	5	0	6	14.36	−15.28	−13.56	−14.42	−0.06
π	5	π	6	π	5	π	6	14.27	−13.92	−13.60	−13.76	0.51
0	5	π	6	0	5	π	6	14.39	−15.28	−13.60	−14.44	−0.05
0	5	0	6	0	6	0	5	1.56	− 1.81	− 1.81	− 1.81	−0.25
π	5	π	6	π	6	π	5	1.51	− 1.68	− 1.68	− 1.68	−0.17
0	5	π	6	π	6	0	5	1.35	− 1.37	− 1.37	− 1.37	−0.02

[a] The value of k and the band index of electron 1 before scattering.
[b] The same values for electron 2 before scattering.
[c] The same values for electron 1 after scattering.
[d] The same values for electron 2 after scattering.
[e] The attractive term for electron 1.
[f] The attractive term for electron 2.

bonds $\lambda = 173$ mμ, and finally for the C-O bond $\lambda = 157$ mμ.

III. RESULTS

In Table II we give the quantities C, A_1, A_2, $\tilde{A}$, and Δ for different wave numbers and band indices 4, 5, and 6, respectively of electrons 1 and 2 for the cytosine molecule in eV units.[24] It is easy to show from the band structure of poly-C[11] that the fifth band is the valence (highest filled) band and the sixth one is the conduction (lowest unfilled) band.

IV. DISCUSSION

From Table II we can see that in the case of the narrow second-highest filled band (the fourth band, which has[11] a width of 0.03 eV), if the initial and final states for all electrons are the same, the absolute value of the attractive term is more than 3 eV larger than that of any of the Coulomb terms (see the first three rows of the Table II). If electrons 1 and 2 change their momenta during the scattering process (see the fourth row of the Table), then Δ is only ~ -0.5 eV for this band. (It should be mentioned that for all three bands considered, the upper band edge lies at $ak = 0$ and the lower one at $ak = \pi$.)

In the case of the valence band (band 5, which has a width of 0.31 eV: the gap between band 4 and 5 is[11] 0.52 eV; see the fifth row of the Table) we have obtained the small value of -0.03 eV for Δ, and in the other three cases (rows 6–8), Δ has positive values between ~ 1.0 and ~ 0.5 eV.

In the case of the conduction band (band 6, with a width of 0.15 eV and a large gap of[11] 4.53 eV from band 5), Δ is positive in all the cases investigated (values of

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[24] In connection with this Table we should like to mention that though the conservation of momentum ($\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2'$) is fulfilled in all the cases investigated, the condition to form Cooper pairs ($k_1 = -k_2$ and $k_1' = -k_2'$) is not fulfilled in every case. In this connection, we have to mention that for a given band the energy value and the wave function belonging to $ak = \pi$ are the same as those belonging to $ak = -\pi$. Therefore each $ak = \pi$ value should be understood with both signs. To conserve momentum in the scattering process we have to write, for instance, in the second row $ak_1 = \pm\pi$, $ak_2 = \mp\pi$, $ak_1' = \pm\pi$, and $ak_2' = \mp\pi$. In this way the conditions for Cooper-pair formations are fulfilled in the "0 0 0 0" and "$\pi\ \pi\ \pi\ \pi$" cases, but they are not fulfilled in the "0 π 0 π" or the "0 π π 0" case. Nevertheless, we have performed the calculations also for these cases, in order to have more data for the comparison of C and $\tilde{A}$.

$\sim$2 eV for scattering processes with the same initial and final momenta, but only $\sim$0.9 eV for scattering with exchange of momentum).

Turning now to the second part of the Table, where we have collected the results for interband scattering processes we can see that for processes in which one electron comes from band 4, Δ has again quite large negative values (between -5.29 and -3.65 eV), if the individual electrons conserve their momenta and band. The scattering processes with change of momenta or band (or both) have much smaller absolute values of Δ (between -0.34 and 0.01 eV). On the other hand, in those interband scatterings in which electrons belonging to the valence and conduction bands (bands 5 and 6) are involved, Δ has values around zero (either small negative, or small positive values; see the last six rows of the Table). We can conclude that in the cases investigated, the respective absolute values of C and A differ only by 20% (with the exception of the first three rows below the double line in the middle, where Δ is about 37% of C). This fact does not seem to be accidental.

From these results it seems justifiable to conclude that the possibility of enhanced conductivity at room temperature in some regions of DNA (i.e., the possibility of limited pair condensation) has not been excluded. *Of course, this does not mean that in our opinion DNA is really superconductive. We have had only the aim, in the present oversimplified calculations, of calling attention to this possibility in the case of DNA, and thus inspiring other, more thorough investigations.*

In the future we intend to perform calculations of this type also for other periodic DNA models, using better wave functions. In still later calculations, the effect of side chains and lone pairs of electrons (which may give an important contribution to A) should also be taken into account.

In the case of the DNA double helix, there remains also the possibility that the polarization of the π electrons in one chain may give rise to an effective attractive interaction between the π electrons of the other chain, and *vice versa.* Calculations utilizing this possibility might be performed also.

Of course, all our considerations are valid only within the framework of Little's formalism. In this connection we see, first of all, two problems. On the one hand, we are left with the problem whether the introduction of screening (in Little's[1] case), or the neglect of non-first-neighbor interactions in our case does not produce qualitatively wrong results. In this respect we should like to mention that since a DNA base has the dimensions of 4×4 Å^2, a DNA chain is not a one-dimensional system in a mathematical sense. Kuper[6] has estimated in his paper the effective screening length l_s for a polyene to be $\sim$10 Å. In this estimation he has used the value 1 Å for the radius of the tube with which he has replaced the spins of Little's model polymer. In our case, if we put for the radius of this tube, in the case of a homopolynucleotide as poly-$\mathcal{C}$, the underestimated value of 2 Å, then we obtain for l_s, using Eq. (23) of Ref. 6 the value of $\sim$3.6 Å. Since the distance between two super-imposed bases of DNA is $\sim$3.4 Å, our nearest-neighbor approximation without screening up to this distance seems not to be a very crude approximation from the point of view of screening in the case of poly-$\mathcal{C}$. Further, it should be again mentioned that by neglecting the contributions from the lone pairs and side chains, we have underestimated the attractive term. The finite dimension of the DNA chain perpendicular to the long axis may also reduce the effect of thermodynamic fluctuations, increasing in this way the regions of Cooper-pair formation. In this respect, it should not be forgotten that DNA *in vivo* is surrounded also by a nucleoprotein chain, and is in an aqueous solution containing a high concentration of dissolved organic substances. Since such a solution has a fairly well ordered cybotactic structure, the liquid-crystalline environment of DNA may reduce to a great extent the effect of thermodynamic fluctuations in it.

On the other hand, from theoretical point of view it is not very correct to start from a band structure calculated for a nonsuperconductive state and to use the wave functions obtained in this way for the calculation of the interaction terms important from the point of view of the superconductivity.[25] It would be more correct to perform these two steps of the investigation simultaneously. Work in this line is in progress.

To conclude we should express our opinion that if Little's proposal is valid, a complicated enough polymer containing many heteroatoms, like DNA, would have the largest probability of possessing superconductive regions at room temperature. The possible biological consequences of superconductive regions in DNA will be discussed elsewhere.

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[25] A. Zawadowski (private communication).