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Hybridization of Carbon and Equilibrium Distance

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The CNDO/2 method, an approximate self-consistent molecular orbital theory, has been applied to the calculation of equilibrium distances of the carbon-hydrogen bond and the normal and hypothetical carbon-carbon single or double bonds which are usually considered te-te, tri-tri, di-di and te-tri single bonds or tri-tri and di-di double bonds between carbon hybrids. The electronic interaction energies between non-adjacent atomic orbitals for sigma system considering appropriate carbon hybrids have been estimated. From the results of these calculations, it follows that the carbon-carbon bond length of sigma system is little affected by the types of hydbridization of carbon atoms.

It is noteworthy that the CNDO/2 mthod,[1-3] the self-consistent molecular orbital method based on the neglect of differential overlap for all valence orbitals, leads to generally good agreement with experimental values for the bond lengths and bond angles of di, tri and tetra-atomic molecules. The CNDO/2 treatment satisfies the requirement that the molecular wave function and the orbital energies are invariant under orthogonal transformations of the atomic orbital basis set such as the replacement of *s*, *p* orbitals by hybrids. This type of approximation makes it possible to discuss a relationship between the lengths of single bonds in equilibrium and the types of hybridization of carbon atoms.

The carbon-carbon bond lengths for some conjugated hydrocarbons have been studied with the pi bond order (P_{pi}) - bond length (R) relationship for bonds in equilibrium.[4-6] It must be

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[1] J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, S 129 (1965).

[2] J. A. Pople and G. A. Segal, *ibid.*, **43**, S 136 (1965).

[3] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[4] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc. (London)*, **A251**, 172 (1959).

[5] C. A. Coulson and A. Golebiewski, *ibid.*, **78**, 1310 (1961).

[6] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

remembered that the P_{pl}-R relation is based on the following two assumptions; separability of the sigma and pi energies and localization of sigma bonds formed by the overlap of two hybridized orbitals (localization of sigma electron). These assumptions are generally adopted but they will be avoided in this paper.

The relative importance of pi electron resonance and hybridization in the shortening effect for the bond lengths of conjugated hydrocarbons has been discussed by many investigators. Among others, Mulliken[7] suggested that the bond shortening effect of hybridization is of comparable magnitude to that of conjugation for butadiene C_2–C_3 bond distance, and he estimated the C–C bond length with given types of hybridization to be 1.45 Å for a di-di, 1.51 Å for a tri-tri and 1.54 Å for a te-te C–C single bond. It has been generally accepted that the shortening of the covalent radius in the C–C single bond is due to the increased *s* character in the bond orbital. The shortening of C–H distances for diagonal, trigonal and tetrahedral hybrids of the carbon atom can also be explained by this effect.[8]

However, it appeared of interest to investigate further the problem described above for the following reasons. Since little attention has so far been paid to the sigma electron delocalization effects, it was thought advisable to calculate C–C equilibrium distances for given types of hybrid by the molecular orbital method which explicitly treats sigma and pi orbitals together. The calculations were performed on several hydrocarbons; methane, ethane, propane, butane, ethylene, propylene, butadiene and acetylene. It may be concluded from the results of these calculations that the equilibrium lengths of C–C single bonds are little affected by the hybridization of carbon atoms.

Methods of Calculation

In the CNDO/2 approximation, the molecular orbitals, which are approximated as linear combination of valence atomic orbitals, and their energies can be obtained by solving the appropriate set of secular equations and the corresponding secular matrix. The elements of the SCF energy matrix are given in this method by

$$F_{\mu\mu} = H_{\mu\mu} + \left(P_{\mathrm{AA}} - \frac{1}{2}P_{\mu\mu}\right)\gamma_{\mathrm{AA}} + \sum_{(\mathrm{A}\neq\mathrm{B})} P_{\mathrm{BB}}\gamma_{\mathrm{AB}}, \quad (1)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mathrm{AB}}, \qquad (\mu\neq\nu) \quad (2)$$

$$H_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) - \left(Z_{\mathrm{A}} - \frac{1}{2}\right)\gamma_{\mathrm{AA}} - \sum_{\mathrm{A}\neq\mathrm{B}} Z_{\mathrm{B}}\gamma_{\mathrm{AB}}, \quad (3)$$

$$H_{\mu\nu} = \frac{1}{2}S_{\mu\nu}(\beta^0{}_{\mathrm{A}} + \beta^0{}_{\mathrm{B}}), \quad (4)$$

where $H_{\mu\nu}$ is the matrix element of the one-electron Hamiltonian which includes the kinetic energy and the electrostatic potential energy due to the core, the term $-1/2(I_\mu+A_\mu)$ is the core integral, P_{AA} and $P_{\mu\mu}$ are the atomic and orbital electron densities, respectively, $P_{\ \nu}$ is the orbital bond order, Z_{A} is the core charge of atom A, γ_{AB} is the average electron-repulsion integral, $\beta^0{}_{\mathrm{A}}$ and $\beta^0{}_{\mathrm{B}}$ are empirically determined resonance integrals characteristic of atoms A and B, respectively, and $S_{\mu\nu}$ is the overlap integral between atomic orbitals μ and ν. The derivation of the method and the mathematical definitions of all quantities can be found in the original CNDO paper.[1–3] The total electronic energy of the valence electrons is

$$E_{\mathrm{electronic}} = \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}). \quad (5)$$

The total energy of the molecule is obtained by adding the repulsion energy between cores to the total electronic energy. The repulsion energy between cores is approximated by a point-charge model. The result is

$$E_{\mathrm{total}} = E_{\mathrm{electronic}} + \sum_{\mathrm{A}<\mathrm{B}}\sum Z_{\mathrm{A}}Z_{\mathrm{B}}/R_{\mathrm{AB}}, \quad (6)$$

where R_{AB} is the A–B inter-nuclear distance.

The total energy and wave functions were calculated by varying the particular bonding distance considered, while the other bonds in the molecule were held fixed at their observed equilibrium distances. An equilibrium bond length was determined by minimizing the total energy with respect to the distance.

It was assumed that the hypothetical carbon-carbon equilibrium distances of molecules which include the broken pi bonds can be estimated by the following three types of calculations. The hypothetical carbon-carbon bonds are those which are usually considered to be the tri-tri, di-di and te-tri C–C single bonds or the di-di C–C double bond.

Calculation A. The contribution of pi bonding energies can be eliminated from the total energies of ethylene and acetylene in the manner

$$E^\dagger = E_{\mathrm{total}} - \frac{1}{2}\sum_{\substack{\mu,\nu \\ (\mu\neq\nu)}}{}^{\pi} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}), \quad (7)$$

where the summation $\sum^{\pi}$ is over pi atomic orbitals. Since the summation does not include the term $\mu=\nu$, the energy $E^\dagger$ contains the energies of unpaired electrons in the pi atomic orbitals of carbons. The calculation can be performed under the condition that each pi electron density is equal to the number of atomic valence pi electrons. The treatment is confined to the calculation of ethylene and acetylene, because pi electron densities of larger conjugated hydrocarbons are non-uniformly distributed according to the CNDO/2 calculation.

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7) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959).

8) "An Epistologue on Carbon Bonds," *ibid.*, **17** Nos. 3/4 (1962).

The equilibrium distances of C–C single bond are determined from the $E^{\dagger}$-R relationship.

Calculation B. Another calculation can be performed to estimate C–C single bond lengths. In the first step of calculation, the overlap integrals between pi orbitals are set equal to zero. The degenerate orbitals for pi electrons resulting from this assumption have an unpaired electron. This configuration is an open shell, but the CNDO/2 method which was designed for the closed shell configuration was used in this approximate calculation. The total energies which contain the energies of unpaired pi electrons are used to estimate the bond distances of tri-tri, di-di and te-tri C–C single bonds or di-di C–C double bond.

Calculation C. The population and energy matrices can be transformed to new matrices by the transformation

$$\boldsymbol{M}' = \boldsymbol{OMO}^{-1}, \tag{8}$$

where $\boldsymbol{M}$ is the population ($\boldsymbol{P}$) or energy ($\boldsymbol{F}$ and $\boldsymbol{H}$) matrix, $\boldsymbol{M}'$ is the matrix in the new basis, and $\boldsymbol{O}$ is an orthogonal transformation matrix.

The total electronic energy is invariant under the transformation

$$\begin{aligned} E_{\text{electronic}} &= \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \\ &= \frac{1}{2}\sum_{\mu,\nu} P'_{\mu\nu}(H'_{\mu\nu} + F'_{\mu\nu}) . \end{aligned} \tag{9}$$

Selecting an appropriate transformation matrix, we can separate the off-diagonal matrix elements of the sigma system into two groups. The matrix elements between bonding orbitals —*e.g.* φ_1 and φ_4 in Fig. 1— form one group (group I). The matrix elements between non-bonding orbitals —*e. g.* φ_1 and φ_5—form the other group (group II). The group I matrix elements can be interpreted as representing localized bonds and the group II elements as representing non-localized bonds. In the local bond approximation in which the group II matrix elements are neglected, the total energy E^* is given by

$$E^* = \frac{1}{2}\sum_{\mu,\nu}{}^{*} P'_{\mu\nu}(H'_{\mu\nu} + F'_{\mu\nu}) + \sum\sum_{A<B} Z_A Z_B/R_{AB}\,, \tag{10}$$

where $\sum^*$ describes the summation over the diagonal and the group I matrix elements. The equilibrium bond lengths which are determined by the E^*-R relationship are shifted in comparison with the bond lengths determined by "calculation B."

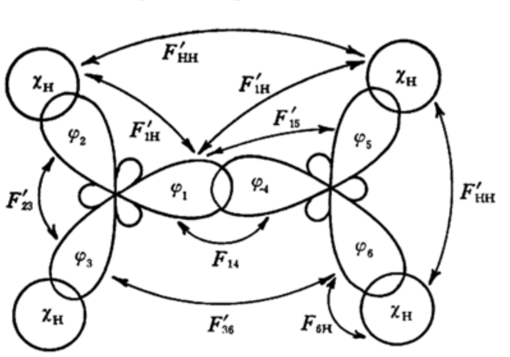

Fig. 1. Energy matrix elements of sigma systems for ethylene.
χ are atomic orbitals of hydrogens.
φ are hybridized orbitals of carbons.
$\boldsymbol{F}$ indicate the matrix elements between the bonding orbitals (group I), $\boldsymbol{F}'$ the matrix elements between the non-bonding orbital (group II).

Results and Discussion

The results of the calculations are given in Tables 1, 2 and 3. The calculated bond lengths are in reasonable agreement with their experimental values. From the calculations, the C–C single bond length is 1.476±0.006 Å, double bond length 1.317 Å, triple bond length 1.198 Å. For the C–H distances of the diagonal, trigonal and tetrahedral carbon hybrids, the agreement between the calculated and observed distances is quite satisfactory. On the basis of this set of data and the transformation properties of the CNDO method, it is felt that the CNDO/2 method is an effective approximate method for determining the relative importance of hybridization and pi electron resonance in the bond shortening effect for conjugated hydrocarbon.

The tri-tri single bond equilibrium distance of ethylene having two unpaired pi electrons was 1.475 Å by "calculation A" and "calculation B." The di-di single bond equilibrium distance of acetylene having four unpaired pi electrons was 1.476 Å. The equilibrium distances of di-di and tri-tri single bonds were longer than that of te-te single bond (ethane) by 0.005 Å and 0.004 Å.

The equilibrium distances of C_1–C_2 and C_2–C_3 single bonds of propylene were 1.487 Å and 1.480Å respectively by "calculation B" in which overlap integrals between pi orbitals were neglected. These equilibrium distances are practically in agreement with that of propane as given in Table 2. The result obtained indicates that the shortening effect for C_1–C_2 bond of propylene is only dependent upon the hyperconjugation between the double bond and the methyl group.

The equilibrium distances of C_1–C_2 and C_2–C_3 single bonds of butadiene having four unpaired pi electrons were 1.482 Å and 1.486 Å respectively by "calculation B" in which all overlap integrals between pi orbitals were set equal to zero. The equilibrium distances of C_1–C_2 and C_2–C_3 bonds of butane were 1.482 Å. The calculated shortening effect for the C_2–C_3 bond of butadiene depends little on hybridization. The results of the calculation indicate that te-te, tri-tri, di-di and te-tri C–C single bonds are substantially in agreement with one another in the range of error in the CNDO/2

TABLE 1. THE EQUILIBRIUM DISTANCES OF CARBON-CARBON BONDS BETWEEN SEVERAL TYPES OF CARBON HYBRIDS FOR C_2 HYDROCARBONS

Type of bond	Equilibrium distance (Å)					
	Single bond			Double bond	Triple bond	Obsd[d]
	CNDO/2	calcd C[b]	calcd C[c]	CNDO/2	CNDO/2	
te-te	1.471	1.621	1.562			1.535 (ethane)
tri-tri	1.475[a]	1.569	1.540	1.317		1.337 (ethylene)
di-di	1.476[a]	1.479	1.452	1.323[a]	1.198	1.205 (acetylene)

a) By "calculation A and B"
b) This calculation neglects the group II matrix elements except the intra-atomic (carbon) matrix elements.
c) This calculation neglects the group II matrix elements.
d) "Interatomic distances" Supplement, Special publication No. 18, The Chemical Society (London)

TABLE 2. EQUILIBRIUM DISTANCES OF CARBON-CARBON BONDS FOR C_3 AND C_4 HYDROCARBONS

Molecule	Equilibrium distances (Å)			
	$R(C_1–C_2)$		$R(C_2–C_3)$	
	calcd	obsd[d]	calcd	obsd[d]
Propane	1.478	1.54	1.478	1.54
Propylene	1.463	1.488	1.332	1.353
$H_3C\text{-}\dot{C}H\text{-}\dot{C}H_2$[a]	1.487		1.480	
Butane	1.482	1.539	1.482	1.539
Butadiene	1.332	1.337	1.447	1.483
$H_2\dot{C}\text{-}\dot{C}H\text{-}\dot{C}H\text{-}\dot{C}H_2$[b]	1.482		1.486	
$H_2C{=}CH\text{-}CH{=}CH_2$[c]	1.323		1.494	

a) C_2-C_3 pi overlap integral was set equal to zero. Methyl carbon was taken as C_1.
b) All overlap integrals between pi orbitals were set equal to zero.
c) C_2-C_3 pi overlap integral was set equal to zero. In the result of this calculation, pi electron densities were non-uniformly distributed.
d) See Ref. d, Table 1.

TABLE 3. CARBON-HYDROGEN EQUILIBRIUM DISTANCES

Molecule	C-H Equilibrium distance (Å)			
	CNDO/2	calcd C[a]	calcd C[b]	obsd[c]
Methane	1.114	1.121	1.108	1.093
Ethane	1.117	1.114	1.085	1.093
Ethylene	1.106	1.102	1.085	1.086
Acetylene	1.088	1.085	1.067	1.058

a) This calculation neglects the group II matrix elements except the intra-atomic (carbon) matrix elements.
b) This calculation neglects the group II matrix elements.
c) See Ref. d, Table 1.

calculation.

The di-di double bond equilibrium distance of acetylene having two unpaired pi electrons was 1.323 Å by "calculation A" and "calculation B." The equilibrium distance of the C_2–C_3 bond of butadiene including two localized double bonds was 1.323 Å by "calculation B" in which the overlap integrals between pi orbitals were set equal to zero except for S_{12} and S_{34} pi overlap integrals. The equilibrium distance of di-di double bond is longer than the tri-tri double bond (ethylene) equilibrium distance by 0.006 Å. The difference is in the range of the error of CNDO calculation for bond distance.

On the basis of this calculation, it seems reasonable to assume that the carbon-carbon bond length is little affected by hybridization of the carbon atom.

From the electron densities of s and p orbitals, the types of hybridization of methane, ethane, ethylene and acetylene were essentially sp^3, sp^3, sp^2 and sp hybrids respectively as given in Table 4.

The population ($\boldsymbol{P}$) and energy ($\boldsymbol{F}$ and $\boldsymbol{H}$) matrices of methane, ethane, ethylene and acetylene were transformed to the new matrices ($\boldsymbol{P}'$, $\boldsymbol{F}'$ and $\boldsymbol{H}'$) with the hybrid basis set (sp^3 sp^2 and sp). In the new matrices, the group II matrix elements represent the electronic interaction energies between new non-bonding orbitals. These group II interaction energies were further classified into the two following types: those between neighboring atoms and those between non-neighboring atoms. The former was termed an N type interaction and the latter an N–N type interaction as given in Table 5.

The N type interaction energies between carbon hybrid and hydrogen were 0.0200 eV, 0.2574 eV, 0.3540 eV and 0.0552 eV for methane, ethane, ethylene and acetylene respectively, and those of N–N types were -0.8010 eV, -0.0332 eV and 0.5910 eV for ethane, ethylene and acetylene respectively.

The interaction energies (N type) between carbon hybrids were -4.6901 eV, -4.6725 eV and -0.8389 eV for ethane, ethylene and acetylene respectively. By minimization of total energies neglecting the group II matrix elements, the carbon-hydrogen equilibrium distances shifted from

TABLE 4. THE ORBITAL ELECTRON DENSITIES OF METHANE, ETHANE, ETHYLENE AND ACETYLENE

Molecule	Interatomic distance (Å)	Orbital electron densities				
		C_s	C_{px}	C_{py}	C_{pz}	H
Methane	1.100 (C-E)	1.0620	0.9953	0.9953	0.9953	0.9880
Ethane	1.471 (C-C)*	1.0037	1.0509	0.9719	0.9719	1.0006
Ethylene	1.320 (C-C)*	1.0485	1.0277	0.9492	1.0000	0.9873
Acetylene	1.200 (C-C)*	1.0980	0.9652	1.0000	1.0000	0.9369

* The C-H distances were held fixed at the observed equilibrium distances. X was taken as C-C sigma axis.

TABLE 5. CARBON-CARBON DISTANCES AND INTERACTION ENERGIES (sum of the group II matrix elements)

Molecule	R(C-C) (Å)	Total energies (eV)		Electronic interaction energies (eV)					
		E_{total}	$E^{\dagger}$ [a]	C (intra)	C-C	C-H N type[b]	C-H N-N type[b]	H-H N type[b]	H-H N-N type[b]
Ethane	1.471	−511.7637		−0.0651×2	−4.6901	0.0429×6	−0.1335×6	0.0881×6	0.0021×6
	1.520	−511.6427		−0.1168×2	−3.7640	0.0263×6	−0.0971×6	0.0840×6	0.0024×6
	1.540	−511.5347		−0.1385×2	−3.4313	0.0194×6	−0.0836×6	0.0825×6	0.0024×6
	1.560	−511.3971		−0.1973×2	−3.1224	0.0126×6	−0.0708×6	0.0811×6	0.0024×6
Ethylene	1.320	−464.2028		−0.3717×2	−4.6725	0.0885×4	−0.0083×4	0.0865×4	−0.0141×4
	1.500	−462.1389	−448.8703	−0.5461×2	−1.9523	0.0303×4	0.0804×4	0.0845×4	−0.0055×4
	1.520	−461.7262	−448.8076	−0.5757×2	−1.7763	0.0235×4	0.0885×4	0.0840×4	−0.0052×4
	1.540	−461.2886	−448.7099	−0.6052×2	−1.6037	0.0167×4	0.0960×4	0.0838×4	−0.0049×4
Acetylene	1.200	−417.2808		−0.5986×2	−0.8389	0.0276×2	0.2955×2		−0.0197×2
	1.430	−412.8186	−383.7426	−0.9477×2	−0.0838	0.0014×2	0.2903×2		−0.0091×2
	1.450	−412.1451	−383.8258	−0.9792×2	−0.0698	0.0016×2	0.2876×2		−0.0087×2
	1.470	−411.4412	−383.8610	−1.0120×2	−0.0603	0.0047×2	0.2846×2		−0.0082×2

[a] $E^{\dagger}$ is defined by Eq. (7).

[b] The N type interaction energies refer to the interactions between the neighboring atoms, the N-N types refer to the interactions between the non-neighboring atoms.

1.114 Å to 1.121 Å, 1.117 Å to 1.114 Å, 1.106 Å to 1.102 Å, 1.088 Å to 1.085 Å for methane, ethane, ethylene and acetylene respectively. Also, the carbon-carbon single bond equilibrium distances in a similar manner shifted from 1.471 Å to 1.621 Å 1.475 Å to 1.569 Å, 1.476 Å to 1.479 Å for ethane, ethylene and acetylene type single bonds respectively. In the calculation described above, the intra-atomic (carbon) off-diagonal elements were not neglected, because these calculations were performed to investigate the precision of the local bond approximation between specific atoms. The results of other types of calculation in which all the group II matrix elements were neglected are listed in Tables 1 and 3.

According to this approximation, the carbon-hydrogen bond distance remained unaltered, but the carbon-carbon single bond distance shifted significantly. The length of carbon-carbon single bond distance is di-di $<$tri-tri$<$te-te. The s character in the hybrids decreases in the same order. The result obtained neglecting the non-localized effect of the sigma electrons agrees with the usual conclusion concerning the equilibrium length of the sigma bond.

The sum total (ε) of the electronic interaction energies between non-adjacent atomic orbitals considering appropriate carbon hybrides is generally effective in stabilizing the molecule, but the effective factor in determining the equilibrium distance is the gradient of variation of the interaction energy ε with the change of the interatomic distance rather than the magnitude of its absolute value.

When the electronic interaction energy ε is neglected in the local bond approximation, the effect on the carbon-hydrogen bond length is negligible. However, for the carbon-carbon bond, the calculated distance lengthens by the neglect of the interaction energy ε because it is effective in shortening the equilibrium distance. Therefore, the idea of localized sigma bonds between pairs of atoms is not appropriate in determining the carbon-carbon bond length.

From a different point of view, however, the result of the calculation in this paper may be an example of defects which are introduced by the CNDO (complete neglect of differential overlap) approximation. If it is the case, it may be due to the following approximations of the CNDO/2 method. The arresting features about approximations of the CNDO/2 method are that the off-diagonal bonding parameters (β^0) are given the same value for resonance integrals between sigma orbitals and those between pi orbitals, the one-center exchange integrals are neglected, and the electronic interaction integrals are assumed to depend only on the atoms and not the actual type of orbital (all electron-repulsion integrals are calculated as coulomb integral involving valence s functions). If the calculated equilibrium distances are shifted by the introduction of one-center exchange integrals which play a crucial role in determining the electron distribution in molecule as mentioned by Cook *et al.*,[9] the problem of this paper should be re-examined by the INDO or NDDO method [1,10] which includes the one-center exchange integrals explicitly.

Conclusion

The CNDO/2 method has been applied in the present work to calculate the equilibrium interatomic distances of the hypothetical carbon-carbon single and double bonds. The equilibrium distances of the tri-tri, the di-di and also the te-tri carbon-carbon single bonds are not much different from the te-te single bond. It is also shown the di-di double bond distance is of almost the same magnitude as the tri-tri double bond distance. These results indicate that the carbon-carbon bond length of sigma system is little affected by the state of hybridization of carbon atom.

The above unexpected conclusion is largely dependent upon the validity of the CNDO/2 method employed in this calculation. It has been generally accepted that the model of localized sigma bonds is appropriate in discussing the equilibrium bond length of the sigma system. We find that this approximation is surely satisfactory for the carbon hybrid-hydrogen bond. For the bonds between carbon hybrids, however, this approximation is not reasonable because the bonds between non-adjacent atomic orbitals are appreciably effective in determining the equilibrium distances.

However, it should be emphasized that the above conclusion is obtained as a result of the CNDO/2 method under specific conditions and the result of further elaborate calculation on the problem of this paper may be a subject for future studies.

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