Towards an Improvement of McLachlan's Method
for Spin Density Calculation

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マクラクランのスピン密度計算法の
改良をめざして

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パイ電子ラジカルのスピン密度計算の簡便法であるマクラクラン法の改良が、試みられる。電子スピンの添字を持つグリーン関数に２つの位置座標から相対および重心座標への変換と類似の変換を施して、ファインマン－ダイソン流の摂動展開と組み合わせると、いくつかの近似方法が、得られる。それら自身は、必ずしも簡便法の範囲内にはないが、そこに現れる諸摂動項を吟味することにより、改良法の可能性が、探求される。

INTRODUCTION

The hyperfine splitting constant from a proton in a pi-electron radical is connected with the spin density on the carbon atom to which the proton is attached through the following simple relation[1]:

$$a = Q\rho,$$

where a and ρ stand for the proton hyperfine splitting constant and the spin density on the carbon atom, respectively, Q being the semi-empirical constant about -23 Gs. It may be said that this proportionality has made spin densities be touchstone of methods of electronic structure calculation. Above all the unrestricted Hartree-Fock(UHF) method[2] is worthy of special mention in the sense that it explains the phenomenon of negative spin densities compactly with the concept of the exchange polarization, putting on one side whether the concept is physical or merely formal. The UHF wave function is not an eigenfunction of S^2, S being the total spin operator, so that the projection after or before the UHF self-consistent procedure is essential in advanced calculations.[3] Those and the other elaborate methods, say the configuration interaction method,[4] have their own significance and without any doubt play a principal role in the development of spin density calculation. We can not, however, despise the existence of concise methods, as McLachlan's one,[5] which give

occasionally better results than what is called rigorous, advanced methods, and are valuable in insight into a nature of the problems concerned with spin densities. Although McLachlan's method in its original form sometimes works surprisingly well, it seems still to be improved. Some modifications have been attempted: Nowakowski showed a few neat modifications,[6] but his recommended scheme involving the self-consistent Hückel method should be said to be already outside the scope of ``modification'' in a sense. Honeybourne's careful considera-tion led us to a correction term, π^*,[7] while he gave a topological approach,[8] which is interesting in understanding characteristics of spin densities. Devolder also reached an expression containing π^*.[9] However, his discussion on the improvement of spin density calculation for odd alternant hydrocarbon radicals is incorrect as pointed out by Honey-bourne.[7]

We think it presumably fruitful to examine the various groupings obtained from different perturbation expansions in order to find an improvement of McLachlan's method. Here it is worth while to mention that the improved method should neither require much more complicated computation than the Hückel one nor involve the self-consistent procedure. In this note, introducing Green's functions in the relevant form to the spin density calcula-tion of pi-electron radicals, we seek for the possibility of improving McLachlan's method through the Feynman-Dyson perturbation expansion. So far attaining no conclusive stage, we would like to regard the prospect obtained there as an encouragement for further works.

HAMILTONIAN AND HÜCKEL ORBITALS

Let us make a start with writing the Hamiltonian for the system of pi-electrons in the fixed nuclear framework in the second quantized form:

$$H = \sum_{pq\sigma} T_{pq} a_{p\sigma}^+ a_{q\sigma} + \frac{1}{2} \sum_{\substack{pqrs \\ \sigma\tau}} V_{qs}^{pr} a_{p\sigma}^+ a_{r\tau}^+ a_{s\tau} a_{q\sigma}, \tag{1}$$

where $a_{p\sigma}^+$ and $a_{p\sigma}$ are, respectively, the creation and annihilation operators for the one-electron quantum state $p\sigma$ which should be labelled by ``atomic'' index p and the spin state σ. In diagonalizing the one-electron operator term the following eigenvalue equation is to be solved.

$$\sum_q T_{pq} C_{jq} = \epsilon_j C_{jp},$$

which gives the Hückel orbital energies $\{\epsilon_j\}$ and coefficients $\{C_{jp}\}$. We can assume that all coefficients $\{C_{jp}\}$ are real. It is not essential here to impose the familiar conditions on $\{T_{pq}\}$ as

$$T_{pq} = \begin{cases} \alpha & \text{independent of } p \text{ for } p=q \\ \beta_{pq} & \text{for } p \text{ and } q \text{ in the first neighbor} \\ 0 & \text{otherwise} \end{cases},$$

though necessary in order to make a few elegant theorems for alternant hydrocarbons hold.[10] Denoting the creation and annihilation operators of the σ-spin electron in the Hückel orbital j, respectively, by $b_{j\sigma}^+$ and $b_{j\sigma}$, we can rewrite (1) as

$$H = H_o + H'$$

with the unperturbed Hamiltonian

$$H_o = \sum_{j\sigma} \epsilon_j b_{j\sigma}^+ b_{j\sigma} \tag{2}$$

and the perturbation

$$H' = \frac{1}{2} \sum_{\substack{j k l m \\ \sigma \tau}} V_{km}^{jl} b_{j\sigma}^+ b_{l\tau}^+ b_{m\tau} b_{k\sigma}.$$

In the rest of this section let us consider a little on the ground state of (2). Starting from m atomic one-electron quantum states, we can construct m Hückel orbitals. Name the orbitals 1, 2, $\cdots\cdots m$, in the increasing order of the orbital energy. If m is odd, we have the neutral radical in which the $(m+1)/2$-th orbital is singly occupied and the lower doubly. For even m the anion and cation radicals are obtained of which singly occupied orbitals are, respectively, located at $m/2+1$ and $m/2$. Note that we can treat the anion and cation radicals from a unified point of view, when the change of the nuclear framework is negligible.

SPIN DENSITIES AND GREEN'S FUNCTIONS

Formally speaking, the spin density on an atom p, ρ_p, is defined as a diagonal element

in the atomic representation of the spin density operator.[1] We can, however, give a very compact expression to that quantity in the field-theoretic language within the scope of our present discussion;

$$\rho_p = \langle 0 | a^+_{p\uparrow} a_{p\uparrow} - a^+_{p\downarrow} a_{p\downarrow} | 0 \rangle ,$$

where the up- and down-spin states are denoted by $\uparrow$ anb $\downarrow$, respctively, $|0\rangle$ standing for the ground state of H. Suppose the doublet radicals of which z component of the spin is $\hbar/2$ hereafter. The above equation is ready to take a different form

$$\rho_p = \sum_{jk} \langle 0 | b^+_{k\uparrow} b_{j\uparrow} - b^+_{k\downarrow} b_{j\downarrow} | 0 \rangle c_{kp} c_{jp} \tag{3}$$

by the transformation that

$$\begin{cases} a^+_{p\sigma} = \sum_j b^+_{j\sigma} c_{jp} \\ a_{p\sigma} = \sum_j b_{j\sigma} c_{jp}. \end{cases}$$

On the other hand, Green's functions are defined as

$$g^\sigma_{jk}(t-t') = -i \langle 0 | \hat{T} b_{j\sigma}(t) b^+_{k\sigma}(t') | 0 \rangle / \langle 0 | 0 \rangle, \tag{4}$$

where $\hat{T}$ is Wick's chronological operator and the operators of time arguments are in the Heisenberg picture. Letting $t-t'$ tend to zero keeping $t-t' < 0$, we obtain from (4) with an infinitesimal positive number, θ,

$$g^\sigma_{jk}(-\theta) = i \langle 0 | b^+_{k\sigma} b_{j\sigma} | 0 \rangle,$$

which immediately converts (3) into

$$\rho_p = -i \sum_{jk} \{ g^\uparrow_{jk}(-\theta) - g^\downarrow_{jk}(-\theta) \} c_{kp} c_{jp} . \tag{5}$$

Obeying the convention to write the Fourier transformation as

$$
\begin{cases}
G_{jk}^{\sigma}(\omega)=\int \mathrm{d}(t-t')\mathrm{e}^{i\omega(t-t')}g_{jk}^{\sigma}(t-t') \\[2mm]
g_{jk}^{\sigma}(t-t')=\dfrac{1}{2\pi}\int \mathrm{d}\omega\,\mathrm{e}^{-i\omega(t-t')}G_{jk}^{\sigma}(\omega),
\end{cases}
\tag{6}
$$

we have

$$
\rho_p=\frac{-i}{2\pi}\sum_{jk}\int \mathrm{d}\omega\,\mathrm{e}^{i\omega\theta}\{G_{jk}^{\uparrow}(\omega)-G_{jk}^{\downarrow}(\omega)\}c_{kp}c_{jp}
$$

in place of (5). Thus the spin density is calculated from the knowledge of Green's functions. It is useful to introduce the matrix notation here. To put $\mathbf{G}^{\sigma}=(G_{jk}^{\sigma}(\omega))$ and $\mathbf{C}_p=(c_{jp}c_{kp})$ results in the expression containing the trace:

$$
\rho_p=\frac{1}{2\pi i}\int \mathrm{d}\omega\,\mathrm{e}^{i\omega\theta}T_r\{\mathbf{G}^{\uparrow}-\mathbf{G}^{\downarrow})\mathbf{C}_p\}.
\tag{7}
$$

We can define the unperturbed Green's functions, $\{d_{jk}^{\sigma}(t-t')\}$, and their Fourier transforms, $\{D_{jk}^{\sigma}(\omega)\}$, likewise in (4) and (6), using the unperturbed ground state and the interaction picture instead of $|0\rangle$ and the Heisenberg picture. But in the unperturbed case the Green's functions for $j\neq k$ vanish. Accordingly we have the diagonal matrix

$$
\mathbf{D}^{\sigma}=(D_{jk}^{\sigma}(\omega))=(\delta_{jk}D_j^{\sigma}(\omega))
$$

with

$$
\begin{cases}
D_j^{\uparrow}(\omega)=(\omega-\omega_j+i\theta\eta(j-f))^{-1} \\[2mm]
D_j^{\downarrow}(\omega)=(\omega-\omega_j+i\theta\eta(j-f+1))^{-1},
\end{cases}
$$

where f means the singly occupied orbital in the unperturbed ground state, $\omega_j=\epsilon_j/\hbar$, and η is the integral variable function of the property that

$$
\eta(z)=\begin{cases}
1 & \text{for } z>0 \\
-1 & \text{for } z\leqq 0.
\end{cases}
$$

Note that the unperturbed Green's functions are "known" functions. The problem is how to expand the Green's function in terms of the unperturbed.

PERTURBATION EXPANSION

Assuming that $|0\rangle$ is attainable from the unperturbed ground state through the Gell-Mann-Low theorem[11] and noting that the Hamiltonian (1) includes no spin-changing term, we have a set of the algebraic equations separated "in appearance" by the spin index in the frequency-dependent form with the Feynman-Dyson perturbation theory;

$$\begin{cases} \mathbf{G}^\uparrow = \mathbf{D}^\uparrow + \mathbf{D}^\uparrow \mathbf{S}^\uparrow \mathbf{G}^\uparrow & (8a) \\ \mathbf{G}^\downarrow = \mathbf{D}^\downarrow + \mathbf{D}^\downarrow \mathbf{S}^\downarrow \mathbf{G}^\downarrow \ , & (8b) \end{cases}$$

where $\mathbf{S}^\sigma$ stands for the proper self-energy part, which really cotains both $\mathbf{D}^\uparrow$ and $\mathbf{D}^\downarrow$. If the self-consistent procedure as replacing $\mathbf{S}^\sigma(\mathbf{D}^\uparrow, \mathbf{D}^\downarrow)$ by $\mathbf{S}^\sigma(\mathbf{G}^\uparrow, \mathbf{G}^\downarrow)$ is performed, (8a) and (8b) intertwine. The first order terms of $\mathbf{S}^\sigma$ come from the coulomb and exchange interactions and are certainly dominant. It is an interesting problem whether or not the terms playing a special role in the spin density calculation exist. This is, however, not investigated here. Taking only the first order self-energy part into account, we have

$$\begin{cases} S_{jk}^\uparrow = \sum_{l=1}^{f-1}(2v_{kl}^{jl} - v_{lk}^{jl})/\hbar + (v_{kf}^{jf} - v_{fk}^{jf})/\hbar & (9a) \\ \\ S_{jk}^\downarrow = \sum_{l=1}^{f-1}(2v_{kl}^{jl} - v_{lk}^{jl})/\hbar + v_{kf}^{jf}/\hbar & . & (9b) \end{cases}$$

The infinite series perturbation expansions (8a) and (8b) together with (9a) and (9b) are expected to give a result competing with that of the configuration interaction method. It is, however, not so transparent to solve

$$\mathbf{G}^\sigma = (\mathbf{D}^{\sigma-1} - \mathbf{S}^\sigma)^{-1}$$

that we invoke the aid of the transformation analogous to that of the two positional coordinates into the relative and center of mass ones:

$$\begin{cases} \mathit{\Delta} \mathbf{G} = \mathbf{G}^{\uparrow} - \mathbf{G}^{\downarrow} & \text{(10a)} \\ \mathbf{G} = (\mathbf{G}^{\uparrow} + \mathbf{G}^{\downarrow})/2 \,, & \text{(10b)} \end{cases}$$

which simplifies (7) a little giving

$$\rho_p = \frac{1}{2\pi i} \int \mathrm{d}\omega e^{i\omega\theta} \mathrm{Tr}(\mathit{\Delta}\mathbf{G}\mathbf{C}_p). \qquad (11)$$

For the unperturbed Green's functions and the self-energy parts likewise we set

$$\begin{cases} \mathit{\Delta}\mathbf{D} = \mathbf{D}^{\uparrow} - \mathbf{D}^{\downarrow} \,) & \text{(12a)} \\ \mathbf{D} = (\mathbf{D}^{\uparrow} + \mathbf{D}^{\downarrow})/2 & \text{(12b)} \end{cases}$$

and

$$\begin{cases} \mathit{\Delta}\mathbf{S} = \mathbf{S}^{\uparrow} - \mathbf{S}^{\downarrow} & \text{(13a)} \\ \mathbf{S} = (\mathbf{S}^{\uparrow} + \mathbf{S}^{\downarrow})/2 \,. & \text{(13b)} \end{cases}$$

The substitution of the reverse transformations of (10), (12), and (13) into the difference between and half the sum of (8a) and (8b) results in

$$\begin{cases} \mathit{\Delta}\mathbf{G} = \mathit{\Delta}\mathbf{D} + (\mathbf{D}\mathit{\Delta}\mathbf{S} + \mathit{\Delta}\mathbf{D}\mathbf{S})\mathbf{G} + (\mathbf{D}\mathbf{S} + \mathit{\Delta}\mathbf{D}\mathit{\Delta}\mathbf{S}/4)\mathit{\Delta}\mathbf{G} & \text{(14a)} \\ \mathbf{G} = \mathbf{D} + (\mathbf{D}\mathbf{S} + \mathit{\Delta}\mathbf{D}\mathit{\Delta}\mathbf{S}/4)\mathbf{G} + (\mathbf{D}\mathit{\Delta}\mathbf{S} + \mathit{\Delta}\mathbf{D}\mathbf{S})\mathit{\Delta}\mathbf{G}/4, & \text{(14b)} \end{cases}$$

which is, of course, completely equivalent to (8) in content, and this time $\mathit{\Delta}\mathbf{G}$ and $\mathbf{G}$ explicitly twine together in the infinite perturbation series.

Now let us consider the reduction of a system of equations (14) to the simpler approximate one, examining the terms appearing in the right hand sides of (14a) and (14b) through the replacement of $\mathit{\Delta}\mathbf{G}$ and $\mathbf{G}$ by their zeroth order terms, $\mathit{\Delta}\mathbf{D}$ and $\mathbf{D}$. Since the terms containing $\mathit{\Delta}\mathbf{D}$ doubly are vanishing in the integration for the frequency, $\mathit{\Delta}\mathbf{D}\mathit{\Delta}\mathbf{S}\mathit{\Delta}\mathbf{G}/4$ in (14a) and $\mathit{\Delta}\mathbf{D}\mathbf{S}\mathit{\Delta}\mathbf{G}/4$ in (14b) are the first to be dropped. By the inference, not so reliable as the above, we further omit $\mathbf{D}\mathit{\Delta}\mathbf{S}\mathit{\Delta}\mathbf{G}/4$ and $\mathit{\Delta}\mathbf{D}\mathit{\Delta}\mathbf{S}\mathbf{G}/4$ in (14b): $\mathbf{D}\mathbf{S}$ looks main in

($DS + \Delta D \Delta S/4$) from a formal aspect. The term led by $\Delta D \Delta S/4$ in (14a) being already dead, it seems well-proportioned to replace ($DS + \Delta D \Delta S/4$) by mere DS in (14b). $D \Delta S \Delta G/4$ should throw in its lot with $\Delta D \Delta SG/4$, being as strong as it. Consequently we obtain

$$
\begin{cases}
\Delta G = \Delta D + (D \Delta S + \Delta DS)G + DS \Delta G & \text{(15a)} \\
G = D + DSG & \text{(15b)}
\end{cases}
$$

where no intertwinement of G and ΔG occurs, though G can affect ΔG. This system of equations makes an approximation scheme possible for the general S: Determine G with (15b), substitute it into (15a) to obtain ΔG, and calculate the spin density from (11). This involves the infinite series summation, in other words, the calculation of inverse matrices, and leaps outside our present purpose. We believe that (15) can be confirmed more rigorously.

TOWARDS AN IMPROVEMENT OF McLACHLAN'S METHOD

In this section, considering a few approximation schemes to which (15) is reduced, we attempt to improve McLachlan's method.

The simple Hückel result is given as the roughest approximation by neglecting all the terms expect for ΔD in the right hand side of (15a):

$$
\begin{cases}
\Delta G = \Delta D \\
G: \text{ not concerned,}
\end{cases}
$$

which leads us to the well-known expression

$$
\rho_p = c_{jp}^2 .
$$

If we take $D \Delta SG$ in addition to ΔD in (15a) and ignore DSG in (15b);

$$
\begin{cases}
\Delta G = \Delta D + D \Delta SG & \text{(16a)} \\
G = D & \text{(16b)}
\end{cases}
$$

then under the Pariser-Parr-Pople approximation[12] (11) straightforwardly gives

$$\rho_p = c_{fp}^2 - \frac{1}{2}\sum_r (\pi_{p,r} + \pi_{p,r}^*) c_{fr}^2 \gamma_{rr} - \frac{1}{2}\sum_{(rs)} (\pi_{p,rs} + \pi_{p,rs}^*) c_{fr} c_{fs} \gamma_{rs},$$

where (rs) stands for the r-s bond, γ_{rr} and γ_{rs} being the semi-empirical interelectronic repulsion integrals. Note that the atom-atom and atom-bond polarizabilities here are defined as follows.[13]

$$\pi_{p,r} = 4 \sum_{j=1}^{f-1} \sum_{k=f}^{m} c_{jp} c_{kp} c_{jr} c_{kr} / (\epsilon_j - \epsilon_k),$$

$$\pi_{p,r}^* = 2 \sum_{j=1}^{m}{}' \; c_{fp} c_{jp} c_{fr} c_{jr} / (\epsilon_f - \epsilon_j),$$

$$\pi_{p,rs} = 4 \sum_{j=1}^{f-1} \sum_{k=f}^{m} c_{jp} c_{kp} (c_{jr} c_{ks} + c_{kr} c_{js}) / (\epsilon_j - \epsilon_k),$$

and

$$\pi_{p,rs}^* = 2 \sum_{j=1}^{m}{}' \; c_{fp} c_{jp} (c_{fr} c_{js} + c_{jr} c_{fs}) / (\epsilon_f - \epsilon_j),$$

where the prime on the sigma indicates the exclusion of the f-th term in the summation. Honeybourne[8] is probably the first to refer to the expression like (17). Let us denpte $\beta \pi_{p,r}$ by $\tilde{\pi}_{p,r}$ for a unified β. Taking only the terms led by $\{\pi_{p,r}\}$ into account and replacing $-\gamma_{rr}/2\beta$ by a semi-empirical parameter independent of r, λ, we arrive at the original form of McLachlan's method[5]:

$$\rho_p = c_{fp}^2 + \lambda \sum_r \tilde{\pi}_{p,r} c_{fr}^2. \tag{18}$$

For odd alternant neutral radicals, since $\{\pi_{p,rs} + \pi_{p,rs}^*\}$ and $\{\pi_{p,r}^*\}$ are identically zero, (17) becomes (18) without any approximation. If $\{\pi_{p,r}^*\}$ and $\{\pi_{p,rs}^*\}$ are small enough, we reach (18) approximately for even alternant anion radicals, where $\{\pi_{p,rs}\}$ vanish. Our present definitions of the atom-atom and atom-bond polarizabilities seem to hinder us from giving

such expressions as (18) to cation radicals. Dropping the atom-bond terms in (17), we have

$$\rho_p = c_{fp}^2 + \lambda \sum_r (\tilde{\pi}_{p,r} + \tilde{\pi}_{p,r}^*) c_{fr}^2,$$

which is essentially the same derived by Honeybourne[7)8)] and Dovolder[9)] as modifications of McLachlan's method for neutral radicals. Naturally, this formula is valuable for the radicals of influential $\pi_{p,r}^*$, for example, non-alternant and heteroatomic radicals.

How to go beyond (17) is not very obvious. A few approximation schemes may be possible between (15) and (16). For example, adding $\Delta\mathrm{DSG}$ and $\mathrm{DS}\Delta\mathrm{G}$ to the right hand side of (16a), we obtain

$$\begin{cases} \Delta\mathrm{G} = \Delta\mathrm{D} + (\mathrm{D}\Delta\mathrm{S} + \Delta\mathrm{DS})\mathrm{G} + \mathrm{DS}\Delta\mathrm{G} & (19a) \\ \mathrm{G} = \mathrm{D} & , & (19b) \end{cases}$$

which includes the infinite series only for $\Delta\mathrm{G}$. If we take DSG into account, then a system of equations consisting of the finite series for $\Delta\mathrm{G}$ and the infinite for G,

$$\begin{cases} \Delta\mathrm{G} = \Delta\mathrm{D} + \mathrm{D}\Delta\mathrm{SG} & (20a) \\ \mathrm{G} = \mathrm{D} + \mathrm{DSG} & , & (20b) \end{cases}$$

is obtained in place of (16). Each of (19) and (20) involves the calculation of an inverse matrix, and cannot be a concise method in itself. It will be, of course, suggestive to examine how (19) and (20) work by the practice of calculation and computation, but that seems considerably laborious. Here we like only to look into $\Delta\mathrm{DS}\tilde{\mathrm{D}}$ and $\mathrm{DS}\Delta\mathrm{D}$. These two terms multiplied by C_p give the same trace, which takes the following form after the frequency integration under the Pariser-Parr-Pople approximation.

$$\int d\omega e^{i\omega\theta} \mathrm{Tr}(\Delta\mathrm{DSD}C_p) = \frac{1}{4}\sum_r \pi_{p,r}^* q_r \gamma_{rr} + \sum_{(rs)} \pi_{p,r}^* q_s \gamma_{rs} - \frac{1}{4}\sum_{(rs)} \pi_{p,rs}^* p_{rs} \gamma_{rs}, \qquad (21)$$

where q_r is the charge density on the atom r and p_{rs} is the bond order of the r - s bond;

$$q_r = 2 \sum_{l=1}^{f-1} c_{lr}^2 + c_{fr}^2$$

and

$$p_{rs} = 2 \sum_{l=1}^{f-1} c_{lr} c_{ls} + c_{fr} c_{fs}.$$

The replacement of "$\varDelta \mathbf{G}$ in the right hand side" by $\varDelta \mathbf{D}$ in (19a) brings us to the following finite expansion, though rather ill-sorted.

$$\begin{cases} \varDelta \mathbf{G} = \varDelta \mathbf{D} + (\mathbf{D} \varDelta \mathbf{S} + \varDelta \mathbf{D} \mathbf{S}) \mathbf{G} + \mathbf{D} \mathbf{S} \varDelta \mathbf{D} & \text{(22a)} \\ \mathbf{G} = \mathbf{D} & \text{(22b)} \end{cases}$$

This makes twice (21) be the additional terms to (17), and we can see, to some extent, the influence of the terms contained in (21) on the spin density. Tentative calculation is now in progress on this line, so we would like to put an end to this note by adding some remarks: The first summed term in the right hand side of (21) is half as large as the terms led by $\{ \pi_{p,r}^* \}$ in the right hand side of (17) in the absolute value and they tend to cancel with each other. This situation certainly favors (18). The second summed term is often comparatively large and does not seem to match with the finite expansion (22). Twice the last is likely to be the first correction term to (18) for odd alternant neutral radicals in which, as already mentioned, $\{ \pi_{p,r}^* \}$ and $\{ \pi_{p,rs} + \pi_{p,rs}^* \}$ identically vanish. The contribution from the atom-bond terms is, in general, not negligible.   *Received October 10, 1979*

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