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# The Use of Perturbation Methods for the Study of the Effects of Configuration Interaction

## II. Variation of the $2^{nd}$ Order Energy Correction in the Series of Linear Polyenes and Polyacenes

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The second order contribution to $\pi$ correlation energy of linear polyenes and polyacenes is studied in two partitions of the C.I. matrix, starting from delocalized Molecular Orbitals. When one uses the classical partition $H = H_{SCF} + V$, the correlation energy increases proportionnal to the number of electrons, quite independently of the shape of the molecule. Another partition, which insures the perturbation matrix to be zero-diagonal, gives a larger $2^{nd}$ order correlation energy; the difference between the $2^{nd}$ order contributions of these two expressions tends to a constant and is larger for a compact system than for a linear one. The dependence of the correlation energy to the values of bielectronic integrals used at short distances shows that it arises mainly from short range interactions.

Some statistical models of C.I. matrices are proposed on the basis of the results obtained here. They give some interesting results for second order energies but do not seem to be satisfactory for higher orders.

Der Beitrag zweiter Ordnung zur $\pi$-Korrelationsenergie linearer Polyene und Polyacene wird mittels zweier Aufteilungen der CI-Matrix studiert, ausgehend von delokalisierten MO's. Wenn man die klassische Aufteilung $H = H_{SCF} + V$ benutzt, nimmt die Korrelationsenergie proportional der Zahl der Elektronen zu, unabhängig von der Gestalt des Moleküls. Eine andere Aufteilung, bei der die Diagonalelemente der Störungsmatrix verschwinden, gibt einen größeren Beitrag zweiter Ordnung zur Korrelationsenergie. Die Differenz dieser beiden Beiträge geht gegen eine Konstante und ist für kompakte Systeme größer als für lineare Moleküle. Es wird gezeigt, daß die Korrelationsenergie im wesentlichen auf Wechselwirkungen kurzer Reichweite zurückgeführt werden kann. Einige statistische Modelle für CI-Matrizen werden auf der Grundlage der hier erhaltenen Resultate vorgeschlagen. Sie scheinen für Energien zweiter Ordnung interessant zu sein, jedoch nicht für höhere Ordnungen.

On étudie la contribution du 2è ordre à l'énergie de corrélation $\pi$ de polyènes et polyacènes linéaires pour deux partitions différentes de la matrice d'Interaction de Configuration (IC); on utilise des orbitales moléculaires délocalisées. Quand on emploie la partition classique $H = H_{SCF} + V$, l'énergie de corrélation au 2è ordre croît proportionnellement au nombre d'électrons, indépendamment de la forme de la molécule. Une autre partition, pour laquelle la matrice de l'opérateur de perturbation a ses éléments diagonaux nuls, donne une énergie de corrélation au 2è ordre plus grande; la différence entre ces deux contributions du 2è ordre tend vers une constante et est plus grande pour une molécule compacte que pour une molécule linéaire. La variation de cette énergie de corrélation (du 2è ordre) en fonction des parametres utilisés pour les courtes distances montre que cette énergie provient surtout d'interactions *à* courte distance.

On considère divers modèles statistiques de matrices d'IC fondés sur les résultats précédemment décrits. Ces modèles fournissent des résultats intéressants en ce qui concerne l'énergie de perturbation du 2è ordre, mais ils ne donnent pas satisfaction aux ordres supérieurs.

## 1. Introduction

Møller and Plesset have proposed in 1934 [9] to treat the correlation problem by use of the Rayleigh-Schrödinger expansion, and have derived an expression of the second order correlation energy. In 1955 Nesbet [10] used a similar idea for a configuration interaction problem. Perturbation technique has been applied to a few cases in a priori calculations of small atoms and molecules (Kirgnitz [7], Kelly [6], Grimaldi [4]), with reasonable success: one seems to get about 90% of the correlation energy corresponding to the choosen basis.

On the other hand, Brueckner has studied the respective convergence of Brillouin-Wigner and Rayleigh-Schrödinger expansions for the correlation problem in a free electrons gas [1]. He was able to conclude that when the number $N$ of interacting particles increases, the second and higher order energy corrections are independent of $N$ in the B.W. expansion and remain proportionnal to $N$ when one uses the Rayleigh Schrödinger expansion. In his recent study on $N_2$ Grimaldi has shown that the convergence rate of the R.S. expansion is much better than that of the B.W. development. Thus, the superiority of the R.S. expansion seems well established both by its asymptotic behaviour, and by its efficiency on small systems.

But the R.S. expansion is not uniquely defined. Most of the authors quoted have used the classical partition [hereafter called Møller-Plesset (M.P.) partition]:

$$H = H_{exact} = H^{\text{SCF}} + V$$

and have taken $H^{\text{SCF}}$ as zeroth order Hamiltonian and $V$ as a perturbation operator. In that case the "transition energies" involved in the denominators of the R.S. expansion, are the differences between the eigenvalues of $H^{\text{SCF}}$, and appear consequently as differences between monoelectronic energies. However it is well-known in H.F. theory that such an approximation gives poor values for the spectroscopic transition energies. They are much improved by the inclusion of first order correlation corrections. Thus for a $\pi$ electron problem Nesbet [10] used in the denominators, instead of

$$\langle 0 \mid H^{\text{SCF}} \mid 0 \rangle - \langle i \mid H^{\text{SCF}} \mid i \rangle \tag{1}$$

the differences

$$\langle 0 \mid H \mid 0 \rangle - \langle i \mid H \mid i \rangle = \langle 0 \mid H^{\text{SCF}} \mid 0 \rangle - \langle i \mid H^{\text{SCF}} \mid i \rangle - \langle i \mid V \mid i \rangle \tag{2}$$

$$(\langle 0 \mid V \mid 0 \rangle \text{ being equal to o by definition of } H^{\text{SCF}})\,.$$

Seeing that the second-order Rayleigh-Schrödinger correction gives poor results, Kelly [6] found it necessary to sum an infinite series of contributions belonging to higher terms (which leads to sum an infinite series of diagrams). This is equivalent to the use of modified denominators in second order terms [2].

We have demonstrated that such an expansion, first proposed by P. S. Epstein [3] and here after called Epstein-Nesbet (E.N.) expansion, was a particular R.S. expansion corresponding to a different partition of the total Hamiltonian [2]. Here the unperturbed Hamiltonian is:

$$H_0' = H^{\text{SCF}} + \sum_i \langle i \mid V \mid i \rangle \mid i \rangle \langle i \mid \tag{3}$$

and the modified perturbation Hamiltonian is

$$V' = V - \sum_i \langle i \mid V \mid i \rangle \mid i \rangle \langle i \mid\,. \tag{4}$$

We were able to show that

1. The $2^{nd}$ order correction is always larger in the E.N. expansion than in the classical M.P. expansion (in absolute value);

2. The $3^{rd}$ order correction is always smaller in the E.N. expansion, which insures a faster convergence of that expansion. Epstein-Nesbet series takes in account in its second order, terms appearing in highers orders of the Møller-Plesset series. This seems to be a simpler way to include the corrections of the denominators used by Kelly [6]. We have discussed theoretically and illustrated numerically the importance of that improvement. (For a more general discussion of the possible partitions of the exact Hamiltonian see Steiner [15].)

In the present paper we want to study two different problems. The first one is the asymptotic behaviour of the Rayleigh-Schrödinger expansion for a molecular problem. If one takes localized molecular orbitals it seems likely that when the number $N$ of particles and the dimension of the system increase, the correlation energy will increase roughly proportionnal to $N$, since each of the localized excitations will provide always the same contribution to the total correlation energy. But such a result is not a priori evident when one uses delocalized molecular orbitals. Thus the first purpose of this paper is to study if the use of delocalized molecular orbitals keeps the variation of the second order energy proportionnal to $N$.

The second problem studied here concerns the relative asymptotic behaviour of several R.S. expansions corresponding to different partitions of the exact Hamiltonian.

We also examine here the dependance of correlation energy on the values of the exponent $\xi$ of the Slater orbitals of the basis, and we want to show that the geometrical shape of the molecules (e.g. the degree of connexity of the chemical graph) determines the differences in the asymptotic behaviour between two series of compounds.

To study such problems it is necessary to use a very crude model for molecular systems. This is the reason why we have chosen $\pi$ systems, where the number of atomic orbitals is extremely reduced. In the series of linear polyenes each step implies only an increase of two electrons (four electrons in the series of polyacenes) while a $\sigma$, $\pi$ calculation would imply an increase of at least 10 electrons for each new double bond. Of course we consider our series of conjugated molecules only as a purely formal problem, without any sake of realism in the order of magnitude of the correlation energy per electron, or the values of the transition energies. Thus we did not adjust any parameters. In a given core field we use different sets of atomic $2p_z$ orbitals to build our molecular orbitals.

## 2. Methods

### A) Choice of the Basis

We want to derive here the most compact formula giving the second order correlation energy for a closed shell state. The zeroth order wave function

$$\Psi_0 = | 1 \bar{1} \ldots i \bar{i} \ldots n \bar{n} |$$

is supposed to be self-consistent. One has also a certain number of virtual orbitals $j^*$ used to build excited states. It is not necessary for these orbitals to be the canonical SCF orbitals, which diagonalize the matrix of Lagrange multipliers. In any case, Brillouin's theorem is fulfilled for the "monoexcited" states. Thus, in the second order correlation energy

$$E_0^{(2)} = E_0^{\mathrm{SCF}} + \sum_i \frac{\langle 0 \mid V \mid i \rangle^2}{E_0 - E_i} \tag{5}$$

the states $i$ are the "diexcited" states. However the formulas giving the transition energies are much simpler when one uses the canonical SCF orbitals and later we shall suppose that we start from them.

It is easy to demonstrate [2] that, even for a finite basis of atomic orbitals, one may work either in a basis of single determinants or in a basis of eigenfunctions of $S^2$, provided that for a given space function, one considers all the single determinants with the same $S_z$ eigenvalue and different spin wave functions. The $n^{\text{th}}$ order wave function calculated by a perturbation expansion in a basis of single determinants, differs only from an $S^2$ eigenfunction by $(n+1)^{\text{th}}$ order terms. Thus, as the expression of the matrix elements and of the energies are much simpler in that case, we shall work in a basis of single determinants.

### *B) Matrix Elements and Transition Energies*

We shall use the following notations:

$\left(\begin{smallmatrix} i \\ k \end{smallmatrix} \middle| \begin{smallmatrix} j^* \\ l^* \end{smallmatrix}\right)$ represents the determinant got from the ground state determinant by "excitation" of an electron from the orbital $i$ to the empty orbital $j^*$, and of an electron from the orbital $k$ to the orbital $l^*$. The barred orbitals represent the orbitals occupied by $\beta$ spin electrons.

$(ik \mid j^* \, l^*)$ represents the matrix element of the operator $r_{\alpha\beta}^{-1}$:

$$(ik \mid l\, m) = \left\langle \varphi_i^{(1)} \varphi_k^{(2)} \left| \frac{1}{r_{12}} \right| \varphi_l^{(1)} \varphi_m^{(2)} \right\rangle$$

$$J_{ij} = (ij \mid ij)$$

$$K_{ij} = (ij \mid ji)\,.$$

As usual the $\varepsilon$ are the Hartree-Fock orbital energies.

As the determinants used are eigenfunctions of $H^{\mathrm{SCF}}$,

$$\begin{aligned} \langle \Psi_1 \mid H \mid \Psi_2 \rangle &= \langle \Psi_1 \mid H_0 \mid \Psi_2 \rangle + \langle \Psi_1 \mid V \mid \Psi_2 \rangle \\ &= \langle \Psi_1 \mid V \mid \Psi_2 \rangle\,. \end{aligned}$$

This is why we use indifferently the notations

$$\langle \Psi_1 \mid H \mid \Psi_2 \rangle \text{ or } \langle \Psi_1 \mid V \mid \Psi_2 \rangle\,.$$

A "diexcited" configuration $\left(\begin{smallmatrix} i \\ k \end{smallmatrix} \middle| \begin{smallmatrix} j^* \\ l^* \end{smallmatrix}\right)$ may involve two "excitations" of the same spin or of different spins.

When the two "excitations" are of the same spin, the matrix element is equal to the difference of a coulomb and an exchange integral

$$\left\langle 0 \mid H \mid \left(\begin{smallmatrix} i \\ k \end{smallmatrix} \middle| \begin{smallmatrix} j^* \\ l^* \end{smallmatrix}\right) \right\rangle = (ik \mid j^* \, l^*) - (ik \mid l^* \, j^*)\,. \tag{6}$$

One may verify that the "transition energy" corresponding to such a "diexcited" configuration is:

$$\begin{aligned} E^1_{ikj^*l^*} = \varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k + J_{ik} + J_{j^*l^*} - J_{kl^*} - J_{ij^*} - J_{kj^*} - J_{il^*} - \\ - K_{ik} - K_{j^*l^*} + K_{ij^*} + K_{kl^*} + K_{il^*} + K_{kj^*}\,. \end{aligned} \tag{7}$$

Remembering that the two excitations may involve $\beta$ spin orbitals as well as $\alpha$ the contributions of that type lead to the summation

$$-2\sum_{i<k}\sum\sum_{j^*<l^*}\sum\frac{[(ik\mid j^*l^*)-(ik\mid l^*j^*)]^2}{E^1_{ikj^*l^*}}\,. \tag{8}$$

The two excitations may be of different spin, for instance in the "diexcited" configuration $\left(\frac{i}{k}\middle|\frac{j^*}{l^*}\right)$. For such a configuration, the matrix element with the ground state is equal to

$$\langle 0\mid H\mid\left(\frac{i}{k}\middle|\frac{j^*}{l^*}\right)\rangle=(ik\mid j^*l^*)\,. \tag{9}$$

And the transition energy is equal to

$$\begin{aligned}E^2_{ikj^*l^*}&=\varepsilon_{j^*}+\varepsilon_{l^*}-\varepsilon_i-\varepsilon_k+J_{ik}+J_{j^*l^*}-J_{kl^*}-J_{ij^*}-J_{kj^*}-J_{il^*}+\\&\quad+K_{ij^*}+K_{kl^*}\,.\end{aligned} \tag{10}$$

One may remark that the configuration $\left(\frac{k}{i}\middle|\frac{l^*}{j^*}\right)$ has the same matrix element with $\Psi^0$ and the same transition energy. On the countrary the "diexcited" configurations $\left(\frac{i}{k}\middle|\frac{l^*}{j^*}\right)$ and $\left(\frac{k}{i}\middle|\frac{j^*}{l^*}\right)$ have a different matrix element:

$$\langle 0\mid H\mid\left(\frac{i}{k}\middle|\frac{l^*}{j^*}\right)\rangle=(ik\mid l^*j^*) \tag{11}$$

and a different transition energy $E^2_{ikl^*j^*}$.

Then the contributions of the configurations with two excitations of different spins can be written:

$$-\sum_i\sum_k\sum_{j^*}\sum_{l^*}\frac{(ik\mid j^*l^*)^2}{E^2_{ikj^*l^*}}\,. \tag{12}$$

But it is easy to see that this may be transformed into $\sum_{i<k}\sum\sum_{j^*<l^*}\sum$ and the total second order contribution is equal to

$$\begin{aligned}E^2_{\mathrm{EN}}=&-2\sum_{i<k}\sum\sum_{j^*<l^*}\sum\frac{[(ik\mid j^*l^*)-(ik\mid l^*j^*)]^2}{E^1_{ikj^*l^*}}+\frac{(ik\mid j^*l^*)^2}{E^2_{ikj^*l^*}}+\frac{(ik\mid l^*j^*)^2}{E^2_{ikl^*j^*}}\\&-2\sum_{i<k}\sum\sum_{j^*}\frac{(ik\mid j^*j^*)^2}{E^2_{ikj^*j^*}}\\&-2\sum_i\sum_{j^*<l^*}\sum\frac{(ik\mid j^*l^*)^2}{E^2_{iij^*l^*}}\\&-\sum_i\sum_{j^*}\frac{(ii\mid j^*j^*)^2}{E^2_{iij^*j^*}}\end{aligned} \tag{13}$$

The corresponding formula in the Møller-Plesset type expansion is much simpler, since all the transition energies are then the same:

$$E^1_{ikj^*l^*}=E^2_{ikj^*l^*}=E^2_{ikl^*j^*}=\varepsilon_{j^*}+\varepsilon_{l^*}-\varepsilon_i-\varepsilon_k \tag{14}$$

then

$$\begin{aligned}-E^2_{\mathrm{MP}}=&\,4\sum_{i<k}\sum\sum_{j^*}\sum_{l^*}\frac{(ik\mid j^*l^*)^2+(ik\mid l^*j^*)^2-(ik\mid j^*l^*)\,(ik\mid l^*j^*)}{\varepsilon_{j^*}+\varepsilon_{l^*}-\varepsilon_i-\varepsilon_k}\\&+2\sum_{i<k}\sum\sum_{j^*}\frac{(ik\mid j^*j^*)^2}{2\varepsilon_{j^*}-\varepsilon_i-\varepsilon_k}+\\&+2\sum_i\sum_{j^*<l^*}\sum\frac{(ii\mid j^*l^*)^2}{\varepsilon_{j^*}+\varepsilon_{l^*}-2\varepsilon_i}+\\&+\sum_i\sum_{j^*}\frac{(ii\mid j^*j^*)}{2(\varepsilon_{j^*}-\varepsilon_i)}\,.\end{aligned} \tag{15}$$

It is convenient to introduce a third approximation, which combines the advantages of Epstein-Nesbet and Møller-Plesset expansions. We may use for the transition energies of any diexcited configuration $\begin{array}{c|c} i & j^* \\ k & l^* \end{array}$, twice the mean value of four transition energies corresponding to the four possible monoexcitations: $i \mid j^*$, $k \mid j^*$, $i \mid l^*$ and $k \mid l^*$. The best possible choice appears to correspond to a transition energy to a "state" intermediate between the singlet and the triplet.

$$\begin{aligned} E^3_{i\,k\,j^*\,l^*} = E_{ikl^*j^*} &= \tfrac{1}{2}\,(E_{ij^*} + E_{il^*} + E_{kj^*} + E_{kl^*}) \\ &= \varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k - \tfrac{1}{2}\,[(J_{ij^*} - K_{ij^*}) + (J_{il^*} - K_{il^*}) + \\ &\quad + (J_{kj^*} - K_{kj^*}) + (J_{kl^*} - K_{kl^*})]\,. \end{aligned} \tag{16}$$

It is clear that this approximation corresponds to a new definition of the non perturbed Hamiltonian and of the perturbation Hamiltonian $V''$. Then the diagonal elements $\langle i \mid V'' \mid i \rangle$ of $V''$ are different from zero when $i$ is an excited state. But they are certainly smaller than the corresponding $\langle i \mid V \mid i \rangle$ and there is a priori no reason that they have all the same sign. Thus, that approximation, which is very convenient since one may use Eq. (16) with $E^3_{i\,k\,j^*\,l^*}$ instead of $\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k$, should give much better results than the M.P. expansion. We call "intermediate expansion" this partition which combines the interests of M.P. and R.S. expansion.

### *C) Remark on the Calculation of Matrix Elements*

The computer time consuming process is the calculation of the matrix elements $(ik \mid j^*\, l^*)$. Their number is about 0,5 $(\alpha - 1)^2 n^4$ if one works with a basis of $N = \alpha n$ atomic orbitals for $2n$ electrons. For instance, the calculation of the second order correlation energy of an anthracene like molecule requires the calculation of about 1.200 matrix elements. It becomes rapidly difficult to study a large molecule with a reasonable computing time.

In general

$$(ik \mid j^*\, l^*) = \sum_p \sum_q \sum_r \sum_s c_{ip}\, c_{kq}\, c_{j^*r}\, c_{l^*s}\, (pq \mid rs)\,. \tag{17}$$

The time needed for the direct calculation of all the $(ik \mid j^*\, l^*)$ by this formula increases as $n^8$.

It is very useful to perform the calculation in four successive steps, introducing intermediate matrices with mixed basis:

$$[(pq \mid rs)] \to [(pq \mid rl\,^*)] \to [(pq \mid j^*\, l^*)] \to [(pk \mid j^*\, l^*)] \to [(ik \mid j^*\, l^*)].$$

Each of these steps needs a time increasing only as $n^5$. The use of this programming trick is necessary to allow an economic calculation of the second order corrections.

## 3. Results

We give in Tab. 1 the correlation energies for the first 6 linear polyenes. We have used the same values of the $Z$ exponent for the calculation of the monocentric coulombic integral and for the coulombic integral between linked atoms. This $\xi$ value has been varied in the different calculations. In any cases, at long distances, the $\xi$ value was taken equal to 1.625. The geometry was based on bond length alternation, with $l_{\mathrm{C=C}} = 1.35$ Å, and $l_{\mathrm{C-C}} = 1.46$ Å. These values of bond lengths are the experimental values for butadiene [5]. We did not investigate, in such a crude model, the effect of the supposed geometry on the $\pi$-correlation and total energies.

### *A) Asymptotic Behaviours*

The first striking result is that, for a given $\xi$ exponent, the Møller-Plesset 2nd order correlation energy increases linearly with the number $n$ of carbon atoms in the chain: it appears very clearly on Fig. 1 and by the fact that the correlation energy per electron is rigourously constant in the series (see Tab. 1). The Epstein-Nesbet 2nd order correlation energy increases with $n$, but the correlation energy per electron decreases slowly when $n$ increases.

Table 1. *Second order contribution to the $\pi$ correlation energy in the series of linear polyenes* $C_n H_{n+2}$

|  |  |  | "correlation energy" |  |  | "correl. energy" per electron |  |  |
|---|---|---|---|---|---|---|---|---|
| $n$ | $Z$ | $\pi$-SCF energy (eV) | M.P. | E.N. | Interm. approx. | M.P. | E.N. | $E_{EN}/E_{MP}$ |
| 4 | 1.625 | — 84.72 | 1.01 | 2.04 | 2.03 | 0.25 | 0.51 | 2.0 |
|  | 1.400 | — 85.67 | 0.58 | 1.17 | 1.16 | 0.14 | 0.29 | 2.0 |
|  | 1.200 | — 85.96 | 0.31 | 0.63 | 0.63 | 0.07 | 0.16 | 2.0 |
|  | 1.045 | — 85.69 | 0.17 | 0.35 | 0.35 | 0.04 | 0.09 | 2.0 |
| 6 | 1.625 | —150.98 | 1.52 | 2.67 | 2.65 | 0.25 | 0.44 | 1.76 |
|  | 1.400 | —152.25 | 0.88 | 1.54 | 1.53 | 0.15 | 0.26 | 1.75 |
|  | 1.200 | —152.51 | 0.47 | 0.83 | 0.83 | 0.08 | 0.14 | 1.76 |
|  | 1.045 | —151.90 | 0.26 | 0.47 | 0.47 | 0.04 | 0.08 | 1.80 |
| 8 | 1.625 | —225.12 | 2.03 | 3.23 | 3.22 | 0.25 | 0.40 | 1.60 |
|  | 1.600 | —226.72 | 1.17 | 1.87 | 1.86 | 0.15 | 0.23 | 1.60 |
|  | 1.200 | —226.93 | 0.64 | 1.02 | 1.02 | 0.08 | 0.13 | 1.59 |
|  | 1.045 | —225.99 | 0.36 | 0.58 | 0.58 | 0.04 | 0.07 | 1.61 |
| 10 | 1.625 | —305.17 | 2.54 | 3.79 | 3.77 | 0.25 | 0.38 | 1.52 |
|  | 1.400 | —307.10 | 1.46 | 2.20 | 2.19 | 0.15 | 0.22 | 1.47 |
|  | 1.200 | —307.27 | 0.80 | 1.20 | 1.20 | 0.08 | 0.12 | 1.50 |
|  | 1.045 | —305.98 | 0.45 | 0.68 | 0.68 | 0.04 | 0.07 | 1.51 |
| 12 | 1.625 | —392.13 | 3.02 | 4.31 | 4.30 | 0.25 | 0.37 | 1.43 |
|  | 1.045 | —392.89 | 0.54 | 0.78 | 0.78 | 0.04 | 0.06 | 1.44 |

The calculated ratios between $E_{EN}$ and $E_{MP}$ could be fitted by the empirical formula:

$$\frac{E_{EN}}{E_{MP}} = 1 + \frac{6.0}{n + 1.86} \,. \tag{18}$$

As $E_{MP} = e_{MP}\, n$ (where $e_{MP}$ is the Rayleigh-Schrödinger correlation energy per electron)

$$E_{EN} = e_{MP}\, n + \frac{n + 1.86}{6.0\, e_{RS}}\, n \,. \tag{19}$$

Thus when $n$ tends to infinity, the difference $E_{EN} - E_{MP}$ tends to a constant equal

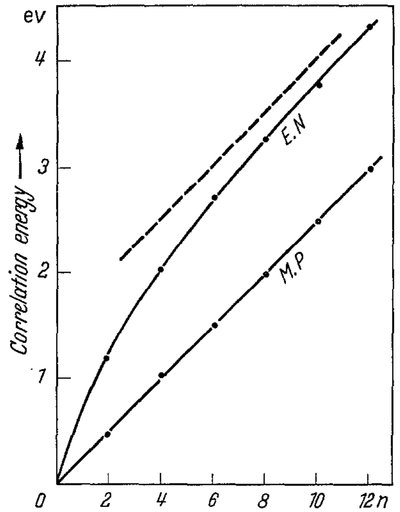

Fig. 1. Correlation energy in the series of linear polyenes ($\xi = 1.625$)

to 6.0 $e_{MP}$. For $\xi = 1.625$ for instance, this constant is equal to 1.5 eV and determines the position of the EN asymptot in Fig. 1.

### *B) Influence of the Reduction of Bielectronic Integrals at Short Distances*

The first main point here is the strong dependence of both EN and MP correlation energies on the values chosen for the short distances bielectronic integrals. This means that *the correlation energy mainly comes from short range interactions*: when one reduces $\xi$ (at short distances only) from 1.625 to 1.045 the correlation energy is divided by 5.8 in the butadiene and becomes nearly negligible. Although the decrease in Coulomb integrals is relatively small, the larger part of correlation energy appears to araise from interactions in the chemical bond. This dominant role of small distances interactions will be explained in a later paper: when one works in a basis of localized SCF MO, the correlation energy mainly comes from "bond excitations" which give contributions proportionnal to $[(pp \mid pp) - (pq \mid pq)]^2$.

It is amazing to plot the SCF $\pi$ electronic energy and the total $\pi$ energy ($E_{\text{SCF}} + E^{(2)}$) as a function of $\xi$ used at short distances (see Fig. 3). It appears

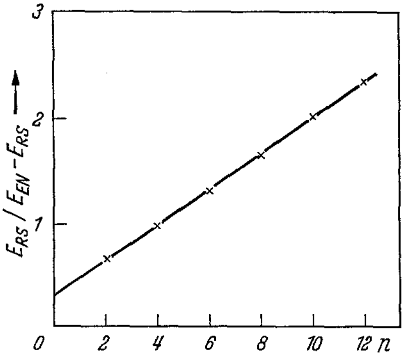

Fig. 2. Analysis of the variation of $E_{\text{EN}}/E_{\text{RS}}$ in the series of linear polyenes

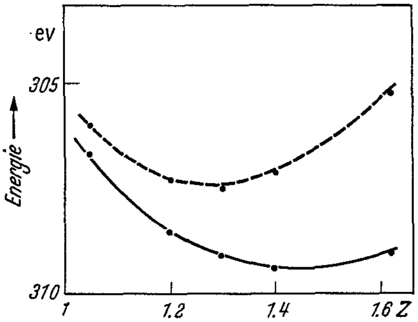

Fig. 3. Variation of the SCF energy (dotted line) and total energy (full line) as a function of the slater exponent ($\xi$) at short distance in $C_{10}H_{12}$

Table 2. *Second order contribution to the $\pi$ correlation energy in the series of linear polyacenes* (in eV)

| | | "correlation energy" | | | "correl. energy" per electron | | |
|---|---|---|---|---|---|---|---|
| | $Z$ | M.P. | E.N. | interm. | M.P. | E.N. | $E_{EN}/E_{MP}$ |
| Benzene | 1.045 | 0.39 | 0.79 | 0.81 | 0.06 | 0.13 | 2.03 |
| | 1.625 | 1.43 | 2.96 | 2.97 | 0.24 | 0.49 | 2.07 |
| Naphtalene | 1.045 | 0.61 | 1.13 | 1.14 | 0.06 | 0.11 | 1.85 |
| | 1.625 | 2.62 | 4.65 | 4.66 | 0.26 | 0.47 | 1.77 |
| Anthracene | 1.045 | 0.89 | 1.54 | 1.56 | 0.06 | 0.11 | 1.73 |
| | 1.625 | 3.62 | 5.94 | 5.95 | 0.26 | 0.43 | 1.64 |

that the correlation energy is of the same order of magnitude than the variation of the SCF energy when $\xi$ changes. But the minima of the two curves do not coincide exactly. This has not a precise meaning in our case since we do not change the monoelectronic integrals but it suggests that the optimisation of $Z$ should be made after a certain Configuration Interaction has been done.

The other striking phenomenon is the complete independence of the ratio $E_{EN}/E_{MP}$ to the reduction of $Z$ at short distances (see Tab. 2). However one must notice that this ratio varies slightly with $Z$ in the series of linear polyacenes (see Tab. 3).

Table 3. *Role of quadruple ($Q$), triple ($T$) and double ($B$) summations of Eq. (13) in the $2^{nd}$ order contribution to the correlation energy of linear polyenes* ($\xi = 1.045$)

| $n$ | $Q$ | $T$ | $D$ | Total |
|---|---|---|---|---|
| 4 | 0.151 | 0.000 | 0.200 | 0.351 |
| 6 | 0.236 | 0.046 | 0.196 | 0.472 |
| 8 | 0.362 | 0.044 | 0.176 | 0.582 |
| 10 | 0.454 | 0.065 | 0.168 | 0.687 |
| 16 | 0.768 | 0.069 | 0.151 | 0.988 |

### *C) Influence of the Shape of the Molecule*

It is interesting to compare the series of linear polyenes and linear polyacenes. In that second series also (see Tab. 2), the Møller-Plesset energy per electron remains constant, and the Epstein-Nesbet energy per electron decreases. But the ratio Epstein-Nesbet energies/MP energy decreases much more slowly than in the series of linear polyenes. It is difficult from only three points to assert that it tends to 1 when $n$ increases to infinity, and the law of variation seems to be more complex.

However one may say that the slower decrease of the Epstein-Nesbet energy per electron is due to the fact that the molecular diagram is more compact than in the series of linear polyenes: while the number of bonds per atom tends to 1 in the series of linear polyenes, it tends to 1.25 in the series of polyacenes.

Another conclusion that may be drawn from Tabs. 1 and 2 concerns the validity of the "Intermediate expansion" on the transition energies. In the two series, the Epstein-Nesbet and "Intermediate" correlation energies never differ by more than 0.02 eV. This confirms the interest of that approximation. One must say however that the agreement is not so good for heteroatomic systems.

## 4. Discussion of the Results

### *A) Statistical Interpretation*

It is really interesting to find such a regularity in the variations of the second order energies with $n$. One may think then that the law empirically found could be theoretically derived. But one does not know any explicit dependance on $n$ of the zeroth-order wave function. One could imagine of course that the second order perturbation energy calculated from the explicit Hückel Molecular Orbital would not lie far from the second order correlation energy and would follow the same laws when $n$ increases. But even then, and with closure approximation the summations seem very difficult to perform.

Within these limits it is possible however to draw some conclusions from the results already got. First one may introduce a simple statistical model of the Configuration Interaction matrix. Let us assume that all the offdiagonal elements of that matrix are equal to $+r$ or $-r$. We also make a closure approximation on the energies: we suppose that the transition energies are equal to $\Delta E$ for the monoexcited states $2\Delta E$ for the diexcited states and so on... If we work in a basis of $\alpha n$ atomic orbitals for a $2n$ electrons problem, the number of molecular integrals in Eq. (15) increases roughly proportionnal to $2n^4(\alpha-1)^2$. Then the second order energy will be about

$$E^{(2)} = \frac{2\,n^4(\alpha-1)^2\,r^2}{2\Delta E}\,. \tag{20}$$

When $n$ varies $r$ and $\Delta E$ change. But if one considers for instance the case of linear polyenes one may verify that the mean value of the transition energies for the monoexcited states is approximatly constant when $n$ increases: it appears clearly from exciton theory [14] that the spectrum of transition energies becomes more dense and broader but remains symmetrical around the $\pi\pi^*$ transition energy for ethylene. Thus we may consider $\Delta E$ is a constant, and we get the law $r = f(n)$. As $E^2 \simeq 2en$ (where $e$ is the correlation energy per electron)

$$r^2 = \frac{2e\,\Delta E}{(\alpha-1)^2\,n^3} \tag{21}$$

$$|r| \simeq C\,n^{-3/2}\,. \tag{22}$$

It seems difficult to verify this law for an arbitrary molecular integral $(ik\mid j^*\,l^*)$. In fact the integrals do not perhaps behave in the same way according to their nature.

Let us examine for instance the behaviour of an integral

$$J_{ij^*} = (ij^*\mid ij^*) \tag{23}$$

involved in the diagonal elements $\langle i\mid V\mid i\rangle$ of the Rayleigh-Schrödinger perturbation theory. We assume that the molecular orbitals $i$ and $j^*$ are such that $|c_{ri}| = |c_{rj^*}| = \frac{1}{\sqrt{n}}$ for all atoms $r$. Then

$$J_{ij^*} = \sum_{p,q}\frac{1}{n^2}\,(pq\mid pq) = \frac{1}{n^2}\,\Sigma\,(pq\mid pq)\,. \tag{24}$$

If we assume that $(pq\mid pq)$ varies as $R^{-1}$, we may use for the atomic integrals the series

$(\lambda, \lambda/2, \lambda/3 \ldots \lambda/n)$. Where $\lambda = (pp, pp)$. Then we must sum the elements of a matrix the superior part of which is equal to

$$(pq \mid pq) = \lambda \begin{bmatrix} 1 & \frac{1}{2} & \frac{1}{3} \cdots & \frac{1}{n} \\ & 1 & \frac{1}{2} \cdots & \frac{1}{n-1} \\ & & \ddots & \vdots \\ & & & 1 \ \frac{1}{2} \\ & & & 1 \end{bmatrix} \tag{25}$$

$$\begin{aligned} \Sigma\,(pq \mid pq) &= \lambda \left(n + \frac{n-1}{2} + \frac{n-2}{3} + \ldots + \frac{n-k}{k+1} + \ldots + \frac{1}{n}\right) \\ &= \lambda \sum_{k=0}^{n-1} \frac{n-k}{k+1} = \lambda \left[ n \sum_{k=0}^{n-1} \frac{1}{k+1} - \sum_{k=0}^{n-1} \frac{k}{k+1} \right]. \end{aligned} \tag{26}$$

One knows that $\sum\limits_{p=1}^{k} 1/P \simeq \log n + c + 0(1/n)$ where $c \simeq 0.577$ is the Euler's constant

Thus

$$n \sum_{k=0}^{n-1} \frac{1}{k+1} = n(\log n + c) \tag{27}$$

$$\sum_{k=0}^{n-1} \frac{k}{k+1} = \sum_{k=0}^{n-1} \frac{k+1}{k+1} - \sum_{k=0}^{n-1} \frac{1}{k+1} \tag{28}$$

Now

$$= n - (\log n + c)\,.$$

$$\begin{aligned} \sum_{p,q} (pq \mid pq) &= \lambda\,[n(\log n + c) - n + \log n + c] \\ &= \lambda\,[n(\log n + c - 1) + \log n + c]\,. \end{aligned} \tag{29}$$

Thus,

$$J_{ij*} \simeq \lambda \left[ \frac{(\log n + c - 1)}{n} \quad \frac{\log n + c}{n^2} \right] \simeq (pp \mid pp)\,\frac{\log n}{n}\,. \tag{30}$$

Thus all the molecular integrals do not vary following the same law.

This is clear also from the consideration of

$$E^2_{\mathrm{EN}} - E^2_{\mathrm{RS}} \to \text{constant} = a\,.$$

It has been demonstrated elsewhere [8] that

$$E^2_{\mathrm{EN}} - E^2_{\mathrm{RS}} \simeq \sum_i \frac{\langle i \mid V \mid 0\rangle^2 \langle i \mid V \mid i\rangle}{(E_0 - E_i)^2} \tag{31}$$

where $i$ are the diexcited state. Then, we must write in our simple model

$$\begin{aligned} a &= \frac{n^4\, r^2\, \langle i \mid V \mid i\rangle}{(2\Delta E)^2} \\ &= b\,\frac{n}{\Delta E^2}\,\langle i \mid V \mid i\rangle\,. \end{aligned} \tag{32}$$

Thus we find

$$\langle i \mid V \mid i\rangle \simeq d\, n^{-1}\,. \tag{33}$$

Our previous calculation gave $J_{ij*} \simeq \dfrac{\log n}{n}$. There remains a certain discrepancy between these two laws, but both agrees to give a slower variation to the diagonal elements $\langle i \mid V \mid i\rangle$.

These speculations may be verified by the analysis of the contributions of respectively the quadruple, triple, and double summations in Eq. (13). One sees from Tab. 3 that:

1. the quadruple summations are responsible of the linear increase of the second order correction; thus it is reasonable to assume that

$$(ik\mid j^*\,l^*)\simeq Cn^{-3/2}\,;$$

2. the triple summations give a contribution which tends to a constant. This indicates that the elements $(ii\mid j^*\,l^*)$ follow the same law;

3. the double summations contribution also tends to a constant; this result confirms that the integrals $(ii\mid j^*\,j^*)$ follow a $n^{-1}$ variation.

## B) Consequences for Higher Orders

Some interesting results may be got from this crude statistical model. One of them concerns the transition energy and will be demonstrated in another paper [8]. It shows that in the calculation of the second order transition energy (difference between the second order perturbed energies of a mono excited state and of the ground state), the effect of the "tri-and di-excited" states tends to a limit which is equal to twice the correlation energy per electron. In other words, when $n$ is large enough, the transition energy may be calculated by the Configuration Interaction between the monoexcited states, the effect of the higher excited states only lowering the results by a constant.

Other conclusions concern the convergence rate of the perturbation expansion. We have already demonstrated [2] that in the third order Rayleigh-Schrödinger correlation energy the main part comes from the diagonal elements $\langle i\mid V\mid i\rangle$ of the diexcited states. We want to discuss here the possibilities of use of a statistical representation of the Configuration Interaction matrix such analysis have been tempted for nuclear problems [12, 13]. In that case one knows nearly nothing about the structure of the matrix of which one desires the general spectral behaviour. In electronic problems many features are known about the structure of the C.I. matrix and it is possible to deduce some interesting results. We have got so some statistical relations relative to the effect of the "mono-, di- and tri-excited" states on the second order energy of a monoexcited state [8].

We shall focuse our attention here on the effects of higher order terms in the perturbation expansion. We shall use two models of the C.I. matrix. In the two cases we assume as before that all the off-diagonal elements have the same absolute value $r$ and that the transition energies are equal to $p\,\Delta E$ for the $p$-excited states.

In the first model we assume that there is an equal probability for each of diagonal element to be $+r$ or $-r$ as seems intuitively reasonable. We shall demonstrate that such a model is too optimistic and gives a third order contribution which tends to zero when $n$ increases! We recall first that in our case the third order contribution

$$E^{(3)}=\sum_i\sum_{j\neq 0}\frac{\langle 0\mid V\mid i\rangle\langle i\mid V\mid j\rangle\langle j\mid V\mid 0\rangle}{(E_0-E_i)\,(E_0-E_j)}\,. \tag{34}$$

Thus $i$ and $j$ are both diexcited states. They must interact between themselves. One may demonstrate that if there are $n^4$ diexcited states, the matrix that one may build from them has about $n^6$ non zero elements. Then for each term in $E^3$ the absolute value will be $\dfrac{r^3}{4\Delta E^2}$ with equal probability of sign $+$ and $-$, than the variance of each term is $2\left(\dfrac{r^3}{4\Delta E^2}\right)^2$. The mean value of the sum of these $n^6$ terms is equal to zero of course, and the variance is equal to $2n^6\left(\dfrac{r^3}{4\Delta E^2}\right)^2$. Then the standard deviation of the sum is equal to

$$\sigma=n^3\sqrt{2}\,\frac{r^3}{4\Delta E^2}\,. \tag{35}$$

Then if we remember that $r^2=\dfrac{2e\Delta E}{n^3}$ Eq. (25) we have

$$\sigma=\frac{e\sqrt{e}}{\sqrt{\Delta E}}\times\frac{1}{n\sqrt{n}}\,.$$

This result is cleary absurd. The value of the constant $\frac{e\sqrt{e}}{\sqrt{\Delta E}}$ is quite small and anyway the dependancy to $n$ is unrealistic: the contribution of the third order would decrease when $n$ increases. One may generalise that result and show that one gets it also when one uses a gaussian repartition of the matrix elements around zero. Moreover it is possible to demonstrate that the behaviour of the whole sum over the contributions of order larger than 2 is as bad.

Then one may think it useful to introduce a second model in which the probability of any matrix element $\langle i \mid V \mid j \rangle$ is equal to $q$ to be $+r$ and $(1-q)$ to be $-r$. Now the mean value is different from zero. For the third order, the mean value of each term is $(2q-1)\frac{r^3}{(4\Delta E)^2}$, and for the $n^6$ term the mean value is $E^3 = n^6(2q-1)\frac{r^3}{(4\Delta E)^2}$. Using again Eq. (25), we get

$$E^3 = n\sqrt{n}(2q-1)\, e \sqrt{\frac{e}{2\Delta E}}$$

the variance does not depend on $q$, so that the standard deviation previously calculated remains valid. If $q$ is independent of $n$ this new variation is also unsatisfactory: it indicates that the third order correlation energy would increase more quickly than $n$. One may demonstrate that the total sum of the series follow nearly the same law. In such a model the perturbation would converge for any $n$, but would give a bad asymptotic behaviour since the whole correlation energy increases more quickly than the number of particles.

Of course, we could suppose that $q$ is a function of $n$ (for example that $q \to \frac{1}{2}$ as $n \to +\infty$) and find any law we want. But that would only be a phenomenological model. The conclusion of the failure of these two models is that there exist in the Configuration Interaction matrix a certain structure; the signs of the matrix elements are not randomly given: there must be some correlation between the signs of the elements involved in the same products of a given summation. But it is not representable by the assumption that all over the matrix the probability to find positive (or negative) elements is greater than $\frac{1}{2}$.

## 5. Conclusions

The $\pi$ electron system in the series of linear polyenes is of particular interest for the formal analysis of the properties of a theoretical model. The most striking results that we get here for the correlation problem may be summarized in the following way:

1. The use of the classical partition $H = H_{\mathrm{SCF}} + V$ for the perturbation development gives a second order correlation energy absolutly proportionnal to the number of electrons. Thus the use of delocalized molecular orbitals gives a satisfactory asymptotic behaviour, an "a priori" non evident result.

This type of variation with $n$ is the same that the one got from localized orbitals and local excitations [11]. In that approximation for homoatomic systems the second order correlation energy seems to be essentially dependant on the nature of the atom and quite insensitive to the molecular shape.

2. The partition of the Hamiltonian which gives a zero-diagonal perturbation matrix yields larger 2nd order correlation energies. The difference between the two second order energies tends to a constant when the number of particles increases. In that approximation the 2nd order correlation energy is much more sensitive to the molecular shape.

3. The two models have the same dependency on the value of the Slater exponent $\xi$ at short distances. This dependency shows clearly that the correlation

energy comes mainly from short range interactions. This fact should favor the configuration interaction from localized molecular orbitals and local excitations only.

4. Compared with the variations of SCF energies per electron from a compound to another the correlation energy is relatively aspecific. This indicates that for many problems concerning the energy of the ground state (resonance energy, difference between the energies of stereo isomers, rotation barriers) the SCF theory could give the main contribution.

5. The regularities in the variations of 2nd order correlation energies suggest that the configuration interaction matrix could be treated as a statistical matrix. We proposed a simple model and fitted it on the calculated laws. It may give interesting results concerning the variation of 2nd order quantities. Some difficulties arise for higher orders contributions.

The statistical analysis of large CI matrix is just beginning: although it encounters some difficulties in the construction of a satisfactory model, it appears to be an interesting and promising subject, which has never received enough attention in the molecular case, although it has been extensively worked out in nuclear and atomic spectroscopy [12, 13].

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