Theoret. chim. Acta (Berl.) 8, 404—423 (1967)

Use of Perturbation Methods for the Study of Configuration Interaction Effects

III. The Second Order Corrections to Transition Energies

J. P. Malrieu, P. Claverie, and S. Diner

Laboratoire de Chimique Quantique, Institut de Biologie Physico-Chimique, Paris, France

Received May 2, 1967

The second order correction to the energy of the ground state involves a *quadruple* summation over molecular orbitals. We show here that the effect of the "triexcited" configurations on a monoexcited state is cancelled by the effect of most of the "diexcited" states on the ground state. Thus the expression for the 2nd order correlated transition energies implies only *triple* summations over Molecular Orbitals. The singlet-triplet splitting is given by *double* summations. Some very simple rules are given for the choice of the finally useful configurations.

Le calcul de l'énergie de corrélation au 2è ordre pour l'état fondamental implique une sommation *quadruple* portant sur les orbitales moléculaires. Nous démontrons dans cet article que les perturbations énergétiques d'un état monoexcité par les configurations «triexcitées» correspondent exactement à celles apportées au fondamental par la plupart des configurations «diexcitées». Ceci se traduit par un grand nombre de suppressions de termes dans l'expression des énergies de transition modifiées par la corrélation au 2è ordre, de sorte qu'il ne reste plus dans une telle expression que des sommations *triples* sur les orbitales moléculaires. De même, la différence d'énergie singulet-triplet est donnée par des sommations *doubles*. Nous donnons quelques règles trés simples concernant le choix des configurations qui sont en fin de compte nécessaires.

Die Beiträge zweiter Ordnung des Grundzustandes ziehen eine *vierfache* Summation über MO's nach sich. Es wird nachgewiesen, daß der Effekt von „dreifach angeregten" Konfigurationen auf einen einfach angeregten Zustand durch gegenseitige Eliminierung aufgehoben wird ähnlich wie die Wirkung der meisten „zweifach angeregten" Konfigurationen auf den Grundzustand, so daß sich nur eine *dreifache* Summation ergibt. Die Singulett-Triplett-Aufspaltung ist durch eine *Doppel*summe gegeben. Es werden einige sehr einfache Regeln für die Wahl der schließlich benötigten Konfigurationen angegeben.

I. Introduction

Once one recognizes the necessity to overcome the independant particles approximation, and if one wants to follow the classical way of Configuration Interaction, the main problem rapidly becomes the dimension of the complete C.I. matrix. People generally truncate it, without good justifications, to fit it to their computationnal abilities. A long time ago Möller and Plesset [9] have proposed to treat the correlation problem by use of perturbation theory, which seems quite natural if one assumes that the Hartree-Fock Hamiltonian is a good approximation to the exact Hamiltonian. Although Nesbet used a similar idea in 1955 for a π problem [10], one had to wait long time to see some systematic applications of that very simple idea (Kelly [6], Kirgnitz [1], Grimaldi [5], Polak and Paldus [12]).

BRUECKNER has discussed [1] the convergence behaviour of Brillouin-Wigner and Rayleigh-Schrödinger perturbation expansions for the correlation problem in a gas of free electrons. The numerical results of GRIMALDI for N_2 also favor the Rayleigh-Schrödinger expansion [5]. But this expansion is not uniquely defined as we have discussed in another paper [2]. The behaviour of the series when the number of interacting particles tends to infinity was not clear for molecular problems when one uses delocalized molecular orbitals. This has been analysed in a previous paper [3] devoted to the series of linear polyenes and polyacenes.

In that paper we started to consider the large C.I. matrix as a statistical matrix following some laws. Such on approach is well known for the analysis of nuclear and atomic spectra [13]. Here our purpose is not to find the general shape of spectral density, but to investigate the effect of Configuration Interaction on some extreme states. After discussing its influence on the ground state, we try to analyse the effect on the lower monoexcited states.

In this paper we show how the Configuration Interaction acts on the transition energies and that the effect of most of the triexcited states on the monoexcited states is compensated by the effect of corresponding diexcited configurations on the ground state: the only doubly excited configurations which play a significant role on the transition energy to a given monoexcited state are the states which interact with it.

The formulas obtained hereafter lead to some asymptotic results for the series of linear polyenes.

II. Hypotheses and Methods

We start here from a single determinant wave function, assumed to be self-consistent for the ground state. The occupied and virtual molecular orbitals are the canonical orbitals, given by the diagonalisation of the Hamiltonian in the chosen basis of Atomic Orbitals.

The validity of the independent particle model for the ground state is well-known. It is largely based on Brillouin's theorem, and illustrated by the stability theorem [9]. This explains the good convergence of the perturbation treatment for the ground state.

The question is more difficult, and the choice of the zeroth-order wave function more embarrassing for the excited states. In many cases however the excited states built with the virtual orbitals have a sufficient overlap with a true eigenfunction to give a correct idea of the transition energy and intensity, and of the properties of the excited state.

The self-consistent Hamiltonian may be written

$$H_{\mathrm{SCF}} = \sum_i H_{(i)} + C \tag{1}$$

where

$$H_{(i)} = T_{(i)} + \textstyle\sum_j^0 2J_{j(i)}^0 - K_{j(i)}^0 \tag{2}$$

is a monoelectronic Hamiltonian and C a constant which insures for the ground state:

$$\langle \Psi_0 \mid H_{\mathrm{SCF}} \mid \Psi_0 \rangle = \langle \Psi_0 \mid H_{ex} \mid \Psi_0 \rangle \,. \tag{3}$$

The summation $\sum\limits_j^0$ runs over all the molecular orbitals occupied in the ground state. In the independent particle model, the transition energy between the ground state and an excited state $| \Psi_i \rangle$ should be defined as

$$\langle \Psi_i | H_{\mathrm{SCF}} | \Psi_i \rangle - \langle \Psi_0 | H_{\mathrm{SCF}} | \Psi_0 \rangle = E_i^{\mathrm{SCF}} - E_0^{\mathrm{SCF}} . \tag{4}$$

And the SCF energy is the sum of monoelectronic energies: thus if the state $| \Psi_i \rangle$ is monoexcited and corresponds to the "transition" from the orbital p to the virtual orbital q^*

$$E_i^{\mathrm{SCF}} - E_0^{\mathrm{SCF}} = \varepsilon_q^* - \varepsilon_p$$

where ε is a monoelectronic energy. (For canonical orbitals these quantities appear as the diagonal Lagrange multipliers of Hartree's theory, or as the eigenvalues of the SCF Hamiltonian).

One knows that this definition of the "transition energy" only gives poor results. But very often the agreement with experiment becomes quite nice when the transition energy is defined as the difference between the mean values of the exact Hamiltonian for the two wave functions:

$$\begin{aligned} \Delta E_{0\to i} &= \langle \Psi_i | H | \Psi_i \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \\ &= \langle \Psi_i | H_{\mathrm{SCF}} | \Psi_i \rangle + \langle \Psi_i | V | \Psi_i \rangle - \langle \Psi_0 | H_{\mathrm{SCF}} | \Psi_0 \rangle - \langle \Psi_0 | V | \Psi_0 \rangle . \end{aligned} \tag{5}$$

Here V is defined by the classical partition of H_{ex}:

$$V = H_{ex} - H_{\mathrm{SCF}} . \tag{6}$$

From Eq. (3) we may write

$$\langle \Psi_0 | V | \Psi_0 \rangle = 0 \tag{7}$$

and the transition energy is given by

$$\Delta E_{0\to i} = (\sum_p \varepsilon_p)^i - (\sum_p \varepsilon_p)^0 + \langle i | V | i \rangle \tag{8}$$

where $(\sum_p)^i$ is the sum over the molecular orbitals occupied in the state i. This is generally considered as the SCF transition energies. In fact these transition energies are already corrected to first-order by the perturbation potential V.

We shall now proceed to a Rayleigh-Schrödinger expansion, using the "correlation" potential as perturbation Hamiltonian, to calculate the transition energy corrected to the second order by correlation effects. To do this we shall calculate both the ground state and the excited energies to the second order.

We limit ourselves here to a closed shell electronic system. The zeroth order wave function for the ground state is

$$| \Psi_0 \rangle = | 1\bar{1} \ldots i\bar{i} \ldots n\bar{n} | \tag{9}$$

where n is the number of occupied orbitals ($2n$ electrons). We call N the total number of atomic (and thus molecular) orbitals we use.

The 2nd order corrected ground state energy may be written

$$E_0^{(2)} = E^{\mathrm{SCF}} + \sum_i \frac{\langle i | V | o \rangle^2}{E_o^{\mathrm{SCF}} - E_i^{\mathrm{SCF}}} . \tag{10}$$

Here i represents all the excited states which may interact with Ψ_0. Taking into account the Brillouin's theorem, and the fact that V is bielectronic all the states i are diexcited configurations.

Let us consider now a monoexcited state Ψ_{pq^*} corresponding to the transition $p \to q^*$ between canonical *M.* orbitals. Its zeroth-order wave function may be written

$$\Psi_{pq^*} = \frac{1}{\sqrt{2}} \mid 11 \ldots (p\bar{q}^* \pm q^*\bar{p}) \ldots n\bar{n} \mid \tag{11}$$

(+ for a singlet and − for a triplet state).

We first assume that our state is *well separated,* i.e. that the nearest states are far enough, or interact with it weakly enough, so that we may apply a Rayleigh-Schrödinger expansion for non-degenerate states. In other words we need for every state i the conditions

$$\frac{\langle \Psi_{pq^*} \mid V \mid i \rangle}{E_{pq^*} - E_i} = \frac{\langle \Psi_{pq^*} \mid H \mid i \rangle}{E_{pq^*} - E_i} \ll 1 \tag{12}$$

This means that the state Ψ_{pq^*} must keep after Configuration Interaction the main weight in one of the eigenfunctions. This is not always the case. We introduce this hypothesis because this greatly simplifies the demonstration of our theorems. But we show in Appendix A, that the main results remain valid for the (near)-degenerate case.

In the non-degenerate case, the second order corrected energy for the excited state Ψ_{pq^*} is given by

$$E^2_{pq^*} = \langle \Psi_{pq^*} \mid H \mid \Psi_{pq^*} \rangle + \sum_j \frac{\langle j \mid V \mid \Psi_{pq^*} \rangle^2}{E^{\mathrm{SCF}}_{pq^*} - E^{\mathrm{SCF}}_j} \,. \tag{13}$$

Here the summation over j runs a priori over the mono-, di- and tri-excited states. We want to get:

$$\begin{aligned} \Delta E^{(2)}_{pq^*} &= E^{(2)}_{pq^*} - E^{(2)}_0 \\ \Delta E^{C.I}_{pq^*} \simeq \Delta E^{(2)}_{pq^*} &= \Delta E^{\mathrm{SCF}}_{pq^*} + \sum_j \frac{\langle j \mid V \mid \Psi_{pp^*} \rangle^2}{E^{\mathrm{SCF}}_{pq^*} - E^{\mathrm{SCF}}_j} - \sum_i \frac{\langle i \mid V \mid o \rangle^2}{E^{\mathrm{SCF}}_o - E^{\mathrm{SCF}}_i} \,. \end{aligned} \tag{14}$$

One has noticed that the transition energies involved in the denominators are the differences between eigenvalues of the unperturbed Hamiltonian, and thus differences between orbital energies. Doing so, we proceed to a strict Rayleigh-Schrödinger expansion, with $H^0 = H^{\mathrm{SCF}}$. We have shown elsewhere that such a method give poorer results than a variant, that we called Epstein-Nesbet [2], in which the denominators energies are taken as mean values of the exact Hamiltonian. But we do not use it, because the cancellations we demonstrate to occur here would not appear as clearly. We demonstrate however in Appendix B that our demonstration is not absolutely dependant of the use of orbital energies in the denominators: a third approximation exists which combines the formal simplicity and the accuracy.

We shall work in a basis of single determinants, not of eigenfunctions of S^2: only the ground state and the monoexcited state we are interested in are S^2 eigenfunctions. It is easy to demonstrate that the first order perturbed wave function one gets so may only differ by 2nd order terms from the exact (S^2 eigenfunction) solution of the problem.

To demonstrate the theorem of reduction of the summations we must establish first some lemmas which will be useful all along the paper.

III. Lemmas

We shall have to reduce some multiple independant summations to multiple summations where the indices are linked by inequalities. Let us consider a function g depending on four indices ik, $j^* l^*$ where i and k on one hand, j^* and l^* on the other, run over two different sets a and b. We suppose that it obeys the following relations

$$g(ik, j^* l^*) = g(ki, l^* j^*) \tag{15}$$

$$g(ik, j^* l^*) + g(ik, l^* j^*) = f(ik, j^* l^*) \tag{16}$$

where $f(ik, j^* l^*)$ is invariant on any permutation of i and k, j^* and l^*

$$[f(ik, j^* l^*) = f(ik, l^* j^*) = f(ki, j^* l^*) = f(ki, l^* j^*)]\,. \tag{17}$$

Let us consider the quadruple summation:

$$A = \sum_i^a \sum_k^a \sum_{j^*}^b \sum_{l^*}^b g(ik, j^* l^*)\,.$$

It is easy to see that:

$$\begin{aligned}\sum_i^a \sum_k^a \sum_{j^*}^b \sum_{l^*}^b g(ik, j^* l^*) &= 2 \sum_{j<k}^a\sum \sum_{j^*<l^*}^b\sum g(ik, j^* l^*) + g(ik, l^* j^*) \; + \\ &+ 2 \sum_{j<k}^a\sum \sum_{j^*}^b g(ik, j^* j^*) + \\ &+ 2 \sum_i^a \sum_{j^*<l^*}^b\sum g(ii\,, j^* l^*) + \\ &+ \sum_i^a \sum_{j^*}^b g\,(ii, j^* j^*)\,.\end{aligned} \tag{18}$$

We shall need also some relations between free summations and summations with exceptions.

Hereafter we use the simplified notations:

$$\sum_i^{a\,\prime} = \sum_{i,\neq p}^a \qquad\qquad \sum_{j^*}^{b\,\prime} = \sum_{j^*,\neq q^*}^b$$

$$\sum_{i<k}^{a\,\prime}\sum{}' = \underbrace{\sum_{i<k}^a\sum}_{\neq p} \qquad\qquad \sum_{j^*<l^*}^{b\,\prime}\sum{}' = \underbrace{\sum_{j^*<l^*}^b\sum}_{\neq p^*}\,.$$

One has for instance:

$$\sum_i^a f(i) = \sum_i^{a\,\prime} f(i) + f(p) \tag{19}$$

and

$$\begin{aligned}\sum_{i<k}^a\sum \sum_{j^*}^b \sum_{l^*} f(ik, j^* l^*) = {}& \sum_{i<k}^{a\,\prime}\sum{}' \sum_{j^*<l^*}^{b\,\prime}\sum{}' f(ik, j^* l^*) + \\ &+ \sum_{i<k}^{a\,\prime}\sum{}' \sum_{j^*}^{b\,\prime} f(ik, j^* q^*) + \sum_i^{a\,\prime} \sum_{j^*<l^*}^{b\,\prime}\sum{}' f(ip, j^* l^*) + \\ &+ \sum_i^{a\,\prime} \sum_{j^*}^{b\,\prime} f(ip, j^* q^*)\,.\end{aligned} \tag{20}$$

IV. Second Order Correlation Energy for the Ground State

We recall briefly the expression of the second order correlation energy [9]. The "diexcited" configurations are of two types:

a) Two "excitations" of different spins: $\begin{array}{c|c} i & j^* \\ k & l^* \end{array} \quad \begin{array}{c|c} \bar{i} & \bar{j}^* \\ \bar{k} & \bar{l}^* \end{array}$.

These two determinants have the same matrix element with the ground state

$$\langle \Psi_i \mid V \mid \Psi_0 \rangle = \pm \left[(ik \mid j^* \, l^*) - (ik \mid l^* \, j^*) \right]$$

where

$$(ik \mid jl) = \langle i(1) \, k(2) \left| \frac{1}{r_{12}} \right| j(1) \, l(2) \rangle \, .$$

The summation over all these configurations will give:

$$2 \sum_{i<k}^{a}\sum \sum_{j^*<l^*}^{b}\sum \frac{[(ik \mid j^* \, l^*) - (ik \mid l^* \, j^*)]^2}{\varepsilon_j{}^* + \varepsilon_l{}^* - \varepsilon_i - \varepsilon_k}$$

b) Two "excitations" of different spins: $\begin{array}{c|c} i & j^* \\ \bar{k} & \bar{l}^* \end{array} \quad \begin{array}{c|c} \bar{i} & \bar{j}^* \\ k & l^* \end{array}$

For these configurations $\langle \Psi_i \mid H \mid \Psi_0 \rangle = \pm \, (ik \mid j^* \, l^*)$. This corresponds to the summation

$$\sum_{i}^{a}\sum_{k} \sum_{j^*}^{b}\sum_{l^*} \frac{(ik \mid j^* \, l^*)^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k}$$

This summation may be transformed according to Eq. (18), and adding the contributions a) and b) one gets

$$\begin{aligned} E_0^{(2)} = {} & 4 \sum_{i<k}^{a}\sum \sum_{j^*<l^*}^{b}\sum \frac{(ik \mid j^* \, l^*)^2 + (ik \mid l^* \, j^*)^2 - (ik \mid l^* j^*) \, (ik \mid j^* \, l^*)}{\varepsilon_{j^*} + \varepsilon_{e^*} - \varepsilon_i - \varepsilon_k} + \\ & + 2 \sum_{i<k}^{a}\sum \sum_{j^*}^{b} \frac{(ik \mid j^* \, j^*)^2}{2\varepsilon_{j^*} - \varepsilon_i - \varepsilon_k} + \\ & + 2 \sum_{i}^{a} \sum_{j^*<l^*}^{b}\sum \frac{(ii \mid j^* \, l^*)^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - 2\varepsilon_i} + \\ & + \sum_{i}^{a} \sum_{j^*}^{b} \frac{(ii \mid j^* \, j^*)}{2\varepsilon_{j^*} - 2\varepsilon_i} \end{aligned} \tag{21}$$

This quadruple summation needs the calculation of $\frac{1}{2} \, n(n-1) \, (N-n) \, (N-n-1)$ matrix elements. If $N = Kn$, and if n is large enough, this number is about $\frac{K^2 n^4}{2}$. Without reduction of the N^4 bielectronic integrals, the computation time increases as n^8. For large N the second order correlation energy appears as the best result one may get in this way. Even with the present abilities of computers it seems almost impossible to reach the third order which implies the calculation of about $K^4 n^6$ molecular integrals.

We shall now calculate the 2nd order correction to the energy of the excited state Ψ_{pq^*}. This energy $E_{p^*}^{(2)}$ will be decomposed into three parts $E_{pq^*,3}^{(2)}$, $E_{pq^*,2}^{(2)}$, $E_{pq^*,1}^{(2)}$, which are respectively the correction to the energy of pq^* araising from its interaction with "tri-, di- and mono-excited" states.

V. Second Order Correction of the Energy of a Monoexcited State, due to the "Triexcited" Configurations

A „triexcited" configuration $\begin{array}{c|c} i & j^* \\ k & l^* \\ m & n^* \end{array}$ (with all possible spin functions) cannot interact with one of the configuration $p\,\bar{q}^*$ or $q^*\,\bar{p}$, except if i, k, or $m = p$, and j^*, l^* or $n^* = q^*$, and if the two orbitals equal to p and q^* have the same spin function. Thus we must examine several types of "triexcited" configurations:

The three "excitations" have the same spin $\begin{array}{c|c} p & q^* \\ i & j^* \\ k & l^* \end{array}$ or $\begin{array}{c|c} \bar{p} & \bar{q}^* \\ \bar{i} & \bar{j}^* \\ \bar{k} & \bar{l}^* \end{array}$. These two configurations may only interact with one of the two configurations of Ψ_{pq^*}. And the matrix element is equal to

$$\langle i\bar{i}\ldots k\bar{k}\ldots q^*\,\bar{p}\ldots|\,H\,|\ldots j^*\,\bar{i}\ldots l^*\,k\,q^*\,\bar{p}\rangle = (ik\,|\,j^*\,l^*) - (ik\,|\,l^*\,j^*)\,.$$

Taking into account the factor $\frac{1}{\sqrt{2}}$ in Ψ_{pq^*}, these configurations lead to the summation:

$$A = \sum_{i<k}^{a}{}'\sum{}'\;\sum_{j^*<l^*}^{b}{}'\sum{}'\;\frac{[(ik\,|\,j^*\,l^*) - (ik\,|\,l^*\,j^*)]^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k}$$

The two conplementary excitations $\begin{array}{c|c} i & j^* \\ k & l^* \end{array}$ in the tri-excited configuration may be of the same spins but of a different spin than that of the transition $p\,q^*$: we have then the configurations $\begin{array}{c|c} p & q^* \\ \bar{i} & \bar{j}^* \\ \bar{k} & \bar{l}^* \end{array}$ and $\begin{array}{c|c} \bar{p} & \bar{q}^* \\ i & j^* \\ k & l^* \end{array}$. The matrix element

$$\langle \Psi_{pq^*}\,|\,H\,|\,\begin{array}{c|c} p & q^* \\ \bar{i} & \bar{j}^* \\ \bar{k} & \bar{l}^* \end{array}\rangle \text{ is in general equal to:}$$

$\pm\,[(ik\,|\,j^*\,l^*) - (ik\,|\,l^*\,j^*)]$. But if i or $k = p$, and if j^* or $l^* = q^*$ the configuration interacts with the two configurations of Ψ_{pq^*}.

Let us consider thus the configuration $\begin{array}{c|c} p & q^* \\ \bar{p} & \bar{q}^* \\ \bar{i} & \bar{j}^* \end{array}$

$$\langle \Psi_{pq^*}\,|\,H\,|\ldots i\bar{j}^*\ldots q^*\,\bar{q}^*\rangle = \frac{1}{\sqrt{2}}\,[(pi\,|\,q^*\,j^*) - (pi\,|\,j^*\,q^*) \pm (pi\,|\,q^*\,j^*)]$$

$$= \frac{1}{\sqrt{2}}\begin{bmatrix} 2(pi\,|\,q^*\,j^*) - (pi\,|\,j^*\,q^*) \\ \text{or} \\ -(pi\,|\,j^*\,q^*) \end{bmatrix}. \tag{22}$$

Symmetrically

$$\langle \Psi_{pq^*}\,|\,H\,|\ldots j^*\,\bar{i}\ldots q^*\,\bar{q}^*\rangle = \frac{1}{\sqrt{2}}\,[(pi\,|\,q^*\,j^*) \pm (pi\,|\,q^*\,j^*) - (pi\,|\,j^*\,q^*)]$$

$$= \frac{1}{\sqrt{2}}\begin{bmatrix} 2(pi\,|\,q^*\,j^*) - (pi\,|\,j^*q^*) \\ \text{or} \\ (pi\,|\,j^*q^* \end{bmatrix}. \tag{23}$$

We may write then the effect of the configurations $\begin{array}{c|l} p & q^* \\ \bar{i} & \bar{j}^* \\ \bar{k} & \bar{l}^* \end{array}$

$$B = \mathop{\sum{}'\sum{}'}\limits_{i<k}^{a} \mathop{\sum{}'\sum{}'}\limits_{j^*<l^*}^{b} \frac{[(ik \mid j^*\, l^*) - (ik \mid l^*\, j^*)]^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k} +$$

$$+ \sum_{i}^{a}{}' \mathop{\sum{}'\sum{}'}\limits_{j^*<l^*}^{b} \frac{[(ip \mid j^*\, l^*) - (ip \mid l^*\, j^*)]^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_p} +$$

$$+ \mathop{\sum{}'\sum{}'}\limits_{i<k}^{a} \sum_{j^*}^{b}{}' \frac{[(ik \mid j^*\, q^*) - (ik \mid q^*\, j^*)]^2}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_k} +$$

$$+ \sum_{i}^{a}{}' \sum_{j^*}^{b}{}' \begin{bmatrix} (2(ip \mid j^*\, q^*) - (ip \mid q^*\, j^*)^2 \\ \text{or} \\ (ip \mid j^*\, q^*)^2 \end{bmatrix} \frac{1}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_p}$$

The two complementary excitations may be of different spins:

$$\begin{array}{c|l} p & q^* \\ i & j^* \\ \bar{k} & \bar{l}^* \end{array} \text{ and } \begin{array}{c|l} \bar{p} & \bar{q}^* \\ \bar{i} & \bar{j}^* \\ k & l^* \end{array}.$$

One must notice that some of these configurations have already been considered in the previous paragraph:

$$\begin{array}{c|l} p & q^* \\ i & j^* \\ \bar{p} & \bar{q}^* \end{array} \text{ and } \begin{array}{c|l} \bar{p} & \bar{q}^* \\ \bar{i} & \bar{j}^* \\ p & q^* \end{array}.$$

The summation may be written:

$$C = \mathop{\sum{}'\sum{}'}\limits_{i \quad k}^{a} \mathop{\sum{}'\sum{}'}\limits_{j^* \quad l^*}^{b} \frac{(ik \mid j^*\, l^*)^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k} +$$

$$+ \sum_{i}^{a}{}' \mathop{\sum{}'\sum{}'}\limits_{j^* \quad l^*}^{b} \frac{(ip \mid j^*\, l^*)}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_p} +$$

$$+ \mathop{\sum{}'\sum{}'}\limits_{i \quad k}^{a} \sum_{j^*}^{b}{}' \frac{(ik \mid j^*\, q^*)^2}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_k}.$$

Now using the Eq. (18) and analogous relations, it is possible to transform these summations into summations with unequalities.

Then adding A, B, C we get the effect of the "tri-excited" states on Ψ_{pq^*}.

$$E^{(2)}_{pq^*,3} = 4 \mathop{\sum{}'\sum{}'}\limits_{i<k}^{a} \mathop{\sum{}'\sum{}'}\limits_{j^*<l^*}^{b} \frac{(ik \mid j^*\, l^*)^2 + (ik \mid l^*\, j^*)^2 - (ik \mid j^*\, l^*)\,(ik \mid l^*\, j^*)}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k} +$$

$$+ 2 \mathop{\sum{}'\sum{}'}\limits_{i<k}^{a} \sum_{j}^{b}{}' \frac{(ik \mid j^*\, q^*)^2 + (ik \mid q^*\, j^*)^2 - (ik \mid j^*\, q^*)\,(ik \mid q^*\, j^*)}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_k} + \frac{(ik \mid j^*\, j^*)^2}{2\varepsilon_{j^*} - \varepsilon_i - \varepsilon_k} +$$

$$+ 2 \sum_{i}^{a}{}' \mathop{\sum{}'\sum{}'}\limits_{j^*<l^*}^{b} \frac{(ip \mid j^*\, l^*)^2 + (ip \mid l^*\, j^*)^2 - (ip \mid j^*\, l^*)\,(ip \mid l^*\, j^*)}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_p} + \frac{(ii \mid j^*\, l^*)^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - 2\varepsilon_i} +$$

$$+ \sum_{i}^{a}{}' \sum_{j^*}^{b}{}' \frac{(ip \mid j^*\, j^*)^2}{2\varepsilon_{j^*} - \varepsilon_i - \varepsilon_p} + \frac{(ii \mid j^*\, q^*)^2}{\varepsilon_{j^*} + \varepsilon_{q^*} - 2\varepsilon_i} + \frac{(ii \mid j^*\, j^*)^2}{2\varepsilon_{j^*} - 2\varepsilon_i} +$$

$$+ \begin{bmatrix} (2(ip \mid j^*\, q^*) - (ip \mid q^*\, j^*))^2 \\ \text{or} \qquad\qquad\qquad (ip \mid q^*\, j^*)^2 \end{bmatrix} \frac{1}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_p}. \tag{24}$$

VI. Theorem of Cancellation of Quadruple Summations

It is interesting to compare $E^{(2)}_{pq,3}$ and $E^{(2)}_{o}$, i.e. the lowering of the energies of the monoexcited state by the "tri-excited" configurations and of the ground state by the "diexcited" states. It appears clearly from Eq. (21) and (24) that many summations are identical except that there are some restrictions in $E^{(2)}_{pq^*,3}$. Thus one must use the Eq. (20) to calculate $E^{(2)}_{0,2} - E^{(2)}_{pq^*,3}$. The calculation is easy, but long and needs some care. We only give here the final result:

$$
\begin{aligned}
E^{(2)}_0 - E^{(2)}_{pq^*,3} = {} & 2 \sum_{i<k}^{a}{}' \sum{}' \sum_{j^*}^{b}{}' \frac{(ik \mid j^* q^*)^2 + (ik \mid q^* j^*)^2 - (ik \mid j^* q^*)\,(ik \mid q^* j^*)}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_k} + \\
& + 2 \sum_{i}^{a}{}' \sum_{j^*<l^*}^{b}{}' \sum{}' \frac{(ip \mid j^* l^*)^2 + (ip \mid l^* j^*)^2 - (ip \mid l^* j^*)\,(ip \mid j^* l^*)}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_p} + \\
& + \sum_{i}^{a}{}' \sum_{j^*}^{b}{}' \frac{(ip \mid j^* j^*)^2}{2\varepsilon_{j^*} - \varepsilon_i - \varepsilon_p} + \frac{(ii \mid q^* j^*)^2}{\varepsilon_{q^*} + \varepsilon_{j^*} - 2\varepsilon_i} + \\
& + \begin{bmatrix} 3(ip \mid j^* q^*)^2 \\ \text{or} \\ 4(ip \mid j^* q^*)^2 + 3(ip \mid q^* j^*)^2 - 4(ip \mid j^* q^*)\,(ip \mid q^* j^*) \end{bmatrix} \frac{1}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_p} + \\
& + 2 \sum_{i<k}^{a}{}' \sum{}' \frac{(ik \mid q^* q^*)^2}{2\varepsilon_{q^*} - \varepsilon_i - \varepsilon_k} + \\
& + 2 \sum_{j^*<l^*}^{b}{}' \sum{}' \frac{(pp \mid j^* q^*)^2}{\varepsilon_{j^*} + \varepsilon_{q^*} - 2\varepsilon_p} + \\
& + \sum_{i}^{a}{}' \frac{(ii \mid q^* q^*)^2}{2\varepsilon_{q^*} - 2\varepsilon_i} + 2 \frac{(ip \mid q^* q^*)^2}{2\varepsilon_{q^*} - \varepsilon_i - \varepsilon_p} + \\
& + \sum_{j^*}^{b}{}' \frac{(pp \mid j^* j^*)^2}{2\varepsilon_{j^*} - 2\varepsilon_p} + 2 \frac{(pp \mid j^* q^*)^2}{\varepsilon_{j^*} + \varepsilon_{q^*} - 2\varepsilon_p} + \\
& + \frac{(pp \mid q^* q^*)}{2\varepsilon_{q^*} - 2\varepsilon_p} \,.
\end{aligned}
\tag{25}
$$

From this equation it appears clearly that the quadruple summations cancel; actually the summations implied in the calculation of $E^{2}_{pq^*,2}$ are only triple and there are only double summations in the calculation of $E^{2}_{pq^*,1}$.

Now one may formulate the theorem:

While the calculation of the 2nd order correlation energy implies a quadruple summation (i.e. an increase in n^4 of the number of matrix elements) the calculation of the transition energy between the ground state and a monoexcited state only implies triple summations (thus an increase in n^3 of the number of matrix elements to be computed).

VII. Lowering of the Energy of the Monoexcited State by the "Diexcited" Configurations

It is clear that, in general, a "diexcited" configuration $\begin{array}{c|c} i & j^* \\ k & l^* \end{array}$ does not interact with a given monoexcited state $p \mid q^*$. For their matrix element to be non-zero, it is necessary and sufficient that *one* of the occupied orbitals $i, k = p$ *or* that *one* of the empty orbitals $j^*, l^* = q^*$. This means the useful diexcited configurations are (neglecting the spin) $\begin{array}{c|cc|c} p & j^* & i & q^* \\ i & l^* & k & j^* \end{array}$. These configurations may differ by two orbitals, or only one orbital from the monoexcited state (we shall say that they are di- or mono-excited with respect to it).

a) We introduce a preliminary lemma.

The matrix element between a "monoexcited" configuration and a "diexcited" configuration which is "monoexcited" with respect to the first one, may be expressed with the only use of *bielectronic integrals*, provided that the Molecular Orbitals are self-consistent.

Consider $\langle \ldots p\bar{q}^* \ldots i\bar{i} \ldots | H | \ldots p\bar{q}^* \ldots i\bar{j}^* \rangle$. If the MO's derive from a SCF calculation, the Brillouin's theorem implies:

$$\langle \Psi_0 | H | \ldots i\bar{j}^* \ldots \rangle = 0 \,.$$

Then one may use the trick:

$$\langle \ldots p\bar{q}^* \ldots i\bar{i} \ldots | H | \ldots p\bar{q}^* \ldots i\bar{j}^* \ldots \rangle = \langle \ldots p\bar{q}^* \ldots i\bar{i} \ldots | H | \ldots p\bar{q}^* \ldots i\bar{j}^* \ldots \rangle -$$
$$- \langle \Psi_0 | H | \ldots i\bar{j}^* \ldots \rangle = (iq^* \,|\, j^*\, q^*) - (iq^* \,|\, q^*\, j^*) - (ip \,|\, j^*\, p) + (ip \,|\, pj^*) \qquad (26)$$

as results clearly from the comparison of integrals implied in both matrix elements.

In the same way:

$$\langle \ldots p\bar{q}^* \ldots i\bar{i} \,|\, H \,|\, \ldots p\bar{q}^* \ldots j^*\, \bar{i} \rangle = (iq^* \,|\, j^*\, q^*) - (ip \,|\, j^*\, p) \,. \qquad (27)$$

b) The two "excitations" in the "diexcited" configuration may involve the same spin.

Let be the configurations $\begin{array}{c|c} p & j^* \\ i & l^* \end{array}$ and $\begin{array}{c|c} i & q^* \\ k & j^* \end{array}$ (and the β spin analogous). When they differ from Ψ_{pq^*} by two orbitals, these configurations lead to the summations:

$$\sum_{i}^{a}{}' \sum_{j^* < l^*}{}'^{b} \sum{}' \frac{[(pi \,|\, j^*\, l^*) - (pi \,|\, l^*\, j^*)]^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_{q^*}} +$$
$$+ \sum_{i < k}{}'^{a} \sum{}' \sum_{j^*}^{b}{}' \frac{[(ik \,|\, q^*\, j^*) - (ik \,|\, j^*\, q^*)]^2}{\varepsilon_{j^*} + \varepsilon_p - \varepsilon_i - \varepsilon_k} \,.$$

We must add the effect of the analogous configurations $\begin{array}{c|c} p & q^* \\ i & j^* \end{array}$ which only differ by one orbital from Ψ_{pq^*}. According to the preceeding lemna [34], they lead to:

$$\sum_{i}^{a}{}' \sum_{j^*}^{b}{}' \frac{[(iq^* \,|\, j^*\, q^*) - (iq^* \,|\, q^*\, j^*) - (ip \,|\, j^*\, p^*) + (ip \,|\, p\, j^*)]^2}{\varepsilon_{j^*} - \varepsilon_i}$$

Note that the denominators correspond now to monoexcitation energies.

c) The "diexcited" configuration may involve two "excitations" of different spins.

These configurations are of two types $\begin{array}{c|c} p & j^* \\ i & l^* \end{array}$ or $\begin{array}{c|c} i & q^* \\ k & j^* \end{array}$. In the general case ($i, k \neq p$, $j^*, l^* \neq q^*$), these configurations lead to the following contributions

$$A = \sum_{i}^{a}{}' \sum_{j^*}{}'^{b} \sum_{l^*}{}' \frac{(ip \,|\, j^*\, l^*)^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_{q^*}} +$$
$$+ \sum_{i}{}'^{a} \sum_{k}{}' \sum_{j^*}^{b}{}' \frac{(ik \,|\, j^*\, q^*)^2}{\varepsilon_{j^*} + \varepsilon_p - \varepsilon_i - \varepsilon_k} \,.$$

Two orbitals of the "diexcited" state may belong to the orbitals implied in the excitation $p \rightarrow q^*$. We have four possibilities:

$\begin{array}{c|c} p & j^* \\ \bar{p} & \bar{l}^* \end{array}$ $\begin{array}{c|c} i & \bar{q}^* \\ k & \bar{q}^* \end{array}$ $\begin{array}{c|c} p & q^* \\ \bar{i} & \bar{j}^* \end{array}$ $\begin{array}{c|c} p & j^* \\ \bar{i} & \bar{q}^* \end{array}$ (and the inverse functions with respect to the spin) that will be treated successively.

$\alpha)$ $\begin{array}{c|c} p & j^* \\ \bar{p} & \bar{l}^* \end{array}$

$$\left\langle \Psi_{pq^*} \,\middle|\, H \,\middle|\, \begin{array}{c|c} p & j^* \\ \bar{p} & \bar{l}^* \end{array} \right\rangle = \frac{1}{\sqrt{2}} \langle q^* \,\bar{p} \pm p\,\bar{q}^* \mid H \mid \ldots j^* \,\bar{l}^* \ldots \rangle$$
$$= \frac{1}{\sqrt{2}} [(q^* \, p \mid j^* \, l^*) \pm (pq^* \mid j^* \, l^*)] \,. \tag{28}$$

We get from these configurations the following sum:

$$B = \sum_{j^* < l^*}{}^{\prime\, b} \sum{}' \frac{[(q^* \, p \mid j^* \, l^*) \pm (p\, q^* \mid j^* \, l^*)]^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_p - \varepsilon_{q^*}} + \sum_{j^*}^{a}{}' \left\{ \begin{array}{c} (q^* \, p \mid j^* \, j^*)^2 \\ \text{or} \\ 0 \end{array} \right\} \frac{2}{2\varepsilon_{j^*} - \varepsilon_p - \varepsilon_{q^*}}$$

$\beta)$ $\begin{array}{c|c} i & q^* \\ \bar{k} & \bar{q}^* \end{array}$ lead, following the same process, to:

$$C = \sum_{j < k}{}^{\prime\, a} \sum{}' \frac{[(ik \mid pq^*) \pm (ik \mid q^* \, p)]^2}{\varepsilon_{q^*} + \varepsilon_p - \varepsilon_i - \varepsilon_k} + \sum_{i}^{a}{}' \left\{ \begin{array}{c} (ii \mid pq^*)^2 \\ \text{or} \\ 0 \end{array} \right\} \frac{2}{\varepsilon_{q^*} + \varepsilon_p - 2\varepsilon_i}$$

$\gamma)$ $\begin{array}{c|c} p & q^* \\ \bar{i} & \bar{j}^* \end{array}$ only interacts with the configuration $q^* \,\bar{p}$ of Ψ_{pq^*}. One uses the lemma of a) and gets:

$$D = \sum_{i}^{a}{}' \sum_{j^*}^{b}{}' \frac{[(q^* \, i \mid q^* \, j^*) - (pi \mid p\, j^*)]^2}{\varepsilon_{j^*} - \varepsilon_i}$$

$\delta)$ $\begin{array}{c|c} p & j^* \\ \bar{i} & \bar{q}^* \end{array}$ interacts with the two configurations of Ψ_{pq^*}

$$\langle q^* \,\bar{p} \ldots i\bar{i} \mid H \mid j^* \,\bar{p} \ldots i\, \bar{q}^* \rangle = (q^* \, i \mid j^* \, q^*)$$
$$\langle p\, \bar{q}^* \ldots i\bar{i} \mid H \mid j^* \,\bar{p} \ldots i\, \bar{q}^* \rangle = - \langle p\bar{i} \ldots i\bar{q}^* \mid H \mid j^* \,\bar{p} \ldots i\bar{q}^* \rangle$$
$$= - (pi \mid j^* \, p) \,. \tag{29}$$

We thus have the sum:

$$E = \sum_{i}^{a}{}' \sum_{j^*}^{b}{}' \frac{[(q^* \, i \mid j^* \, q^*) \pm (pi \mid j^* \, p)]^2}{\varepsilon_{j^*} - \varepsilon_i} \,.$$

Three orbitals of the diexcited states may be identical to p or q^*. One must examine two cases: $\begin{array}{c|c} p & q^* \\ \bar{i} & \bar{q}^* \end{array}$ and $\begin{array}{c|c} p & q^* \\ \bar{p} & \bar{j}^* \end{array}$ (and the inverse spin functions). In the two cases the diexcited configuration interacts with the two configurations of Ψ_{pq^*}.

$\alpha)$ $\begin{array}{c|c} p & q^* \\ \bar{i} & \bar{q}^* \end{array}$ due to the lemna (27) of a)

$$\langle q^* \,\bar{p} \ldots i\bar{i} \mid H \mid q^* \,\bar{p} \ldots i\bar{q}^* \rangle = (q^* \, i \mid q^* \, q^*) - (pi \mid pq^*)$$
$$\langle p\bar{q}^* \ldots i\bar{i} \mid H \mid q^* \,\bar{p} \ldots i\bar{q}^* \rangle = - \langle p\bar{i} \ldots i\bar{q}^* \mid H \mid q^* \,\bar{p} \ldots i\bar{q}^* \rangle$$
$$= - (pi \mid q^* \, p) \,. \tag{30}$$

And consequently we have:

$$F = \sum_{i}^{a}{}' \frac{[(q^* \, i \mid q^* \, q^*) - (pi \mid pq^*) \mp (pi \mid q^* \, p)]^2}{\varepsilon_{q^*} - \varepsilon_i}$$

β) In the same way for $\begin{array}{c|c} p & q^* \\ \bar{p} & \bar{j}^* \end{array}$

$$\langle q^*\,\bar{p}\ldots \mid H \mid q^*\,\bar{j}^*\ldots\rangle = (q^*\,p \mid q^*\,j^*) - (pp \mid p\,j^*) \tag{31}$$

$$\langle p\,\bar{q}^*\ldots \mid H \mid q^*\,\bar{j}^*\ldots\rangle = (p\,q^* \mid q^*\,j^*) \tag{32}$$

$$G = \sideset{}{'}\sum_{j^*}^{b} \frac{[(q^*\,p \mid q^*\,j^*) - (pp \mid pj^*) \pm (pq^* \mid q^*\,j^*)]^2}{\varepsilon_{j^*} - \varepsilon_p}\,.$$

Finally the configuration $\begin{array}{c|c} p & q^* \\ \bar{p} & \bar{q}^* \end{array}$ only interacts with the singlet state and gives

$$H = 2\,\frac{[(pq^* \mid q^*\,q^*) - (pp \mid q^*\,p)]^2}{\varepsilon_{q^*} - \varepsilon_p}\,.$$

Then we may sum the different contributions $A - H$, transforming the sums $\sum\limits_i \sum\limits_k$ in $\sum\limits_{i<k} \sum$. One gets:

$$\begin{aligned}
E^{(2)}_{pq^*,\,2} = {} & 2 \sideset{}{'}\sum_{i<k}^{a} \sideset{}{'}\sum \sideset{}{'}\sum_{j^*}^{b} \frac{(ik \mid q^*\,j^*)^2 + (ik \mid j^*\,q^*)^2 - (ik \mid j^*\,q^*)\,(ik \mid q^*\,j^*)}{\varepsilon_{j^*} + \varepsilon_p - \varepsilon_i - \varepsilon_k} + \\
& + 2 \sideset{}{'}\sum_{i}^{a} \sideset{}{'}\sum_{j^*}^{b} \sideset{}{'}\sum_{l^*} \frac{(ip \mid j^*\,l^*)^2 + (ip \mid l^*\,j^*)^2 - (ip \mid j^*\,l^*)\,(ip \mid l^*\,j^*)}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_{q^*}} + \\
& + \sideset{}{'}\sum_{i<k}^{a} \sideset{}{'}\sum \frac{(ik \mid p\,q^*)^2 + (ik \mid q^*\,p)^2 \pm 2\,(ik \mid pq^*)\,(ik \mid q^*\,p)}{\varepsilon_{q^*} + \varepsilon_p - \varepsilon_i - \varepsilon_k} + \\
& + \sideset{}{'}\sum_{j^*<l^*}^{b} \sideset{}{'}\sum \frac{(q^*\,p \mid j^*\,l^*)^2 + (q^*\,p \mid l^*\,j^*)^2 \pm 2\,(q^*\,p \mid j^*\,l^*)\,(q^*\,p \mid l^*\,j^*)}{\varepsilon} + \\
& + \sideset{}{'}\sum_{i}^{a} \sideset{}{'}\sum_{j^*}^{b} \frac{(ii \mid j^*\,q^*)^2}{\varepsilon_{j^*} + \varepsilon_p - 2\varepsilon_i} + \frac{(ip \mid j^*\,j^*)^2}{2\varepsilon_{j^*} - \varepsilon_i - \varepsilon_q{}^*} + \\
& + 2\,\{[(iq^* \mid j^*\,q^*) - (ip \mid j^*\,p)]^2 + [(ip \mid pj^*) - (iq^* \mid q^*\,j^*)]^2 + \\
& + [(iq^* \mid j^*\,q^*) - (ip \mid j^*\,p)]\,[(ip \mid pj^*) - (iq^* \mid q^*\,j^*)] + \\
& + [{}^{0}_{2}(ip \mid pj^*)\,(iq^* \mid q^*\,j^*)]\}\,\frac{1}{\varepsilon_{j^*} - \varepsilon_i} + \\
& + \sideset{}{'}\sum_{i}^{a} \frac{[(q^*\,i \mid q^*\,q^*) - (pi \mid pq^*)]^2 + (pi \mid q^*p)^2 \mp (pi \mid q^*\,p)\,[(q^*\,i \mid q^*\,q^*) - (pi \mid pq^*)]}{\varepsilon_{q^*} - \varepsilon_i} \\
& + \begin{bmatrix} (ii \mid pq^*)^2 \\ 0 \end{bmatrix} \frac{2}{\varepsilon_{q^*} + \varepsilon_p - 2\varepsilon_i} + \\
& + \sideset{}{'}\sum_{j^*}^{b} \left\{ \frac{[(pp \mid pj^*) - (q^*\,p \mid q^*\,j^*)]^2 + (pq^* \mid q^*\,j^*)^2 \mp (pq^* \mid q^*\,j^*)\,[(pp \mid pj^*) - (q^*\,p \mid q^*\,j^*)]}{\varepsilon_{j^*} - \varepsilon_p} \right. \\
& \left. + \begin{bmatrix} (q^*\,p \mid j^*\,j^*)^2 \\ 0 \end{bmatrix} \frac{2}{2\varepsilon_{j^*} - \varepsilon_p - \varepsilon_{q^*}} \right\} + \\
& + \begin{Bmatrix} 2\,[(pq^* \mid q^*\,q^*) - (pp \mid q^*\,p)]^2 \\ 0 \end{Bmatrix} \frac{1}{\varepsilon_{q^*} - \varepsilon_p}\,.
\end{aligned} \tag{33}$$

One sees immediatly in that expression that the triple summations are identical at least for the numerators, to the triple summations remaining in $E^{(2)}_0 - E^{(2)}_{pq^*,\,3}$. The denominators are now smaller. This means that most of the terms coming from diexcited configurations in the 2nd order correlation energy for the ground state and which had not been cancelled in the transition energy by the action of the "triexcited" configurations on the monoexcited state, correspond exactly to the "diexcited" configurations which interact with the desired monoexcited state.

VIII. Change in the Energy of the Monoexcited State due to the Interaction with the Other Monoexcited States

In general, the monoexcited configurations $i \mid j^*$ differ from Ψ_{pq^*} by two orbitals. On the contrary the monoexcited configurations $i \mid q^*$ and $p \mid j^*$ only differ from $p \mid q^*$ by one orbital. For this last case it is useful to demonstrate a compact expression of the matrix element with $p \mid q^*$.

Let be, for instance $p \mid j^*$ and $\overline{p} \mid \overline{j}^*$. It is clear that:

$$\langle p\overline{q}^* \mid H \mid j^* \, \overline{p} \rangle = (pq^* \mid j^* \, p) \, .$$

The other terms must be developed:

$$\begin{aligned}\langle q^* \, \overline{p} \mid H \mid j^* \, \overline{p} \rangle &= I_{q^* j^*} + \sum_{k}^{a}{}' \, [2(kq^* \mid kj^*) - (kq^* \mid j^* \, k)] + (q^* \, p \mid j^* \, p) \\ &= I_{q^* j^*} + \sum_{k}^{a} [2(kq^* \mid kj^*) - (kq^* \mid j^* \, k)] - (pq^* \mid pj^*) + \\ &\qquad + (q^* \, p \mid pj^*) \, .\end{aligned} \tag{34}$$

One recognizes here the expression of ε_{pq^*}, the non diagonal Lagrange multiplier:

$$\varepsilon_{q^* j^*} = I_{q^* j^*} + \sum_{k}^{a} 2(kq^* \mid kj^*) - (kq^* \mid j^* \, k) \tag{35}$$

thus:

$$\langle q^* \, \overline{p} \ldots \mid H \mid j^* \, \overline{p} \ldots \rangle = \varepsilon_{q^* j^*} - (pq^* \mid pj^*) + (q^* \, p \mid pj^*) \, . \tag{36}$$

In the same way for $i \mid q^*$

$$\langle \ldots q^* \, \overline{p} \ldots i\overline{i} \mid H \mid \ldots p\overline{p} \ldots q^* \, \overline{i} \rangle = \varepsilon_{ip} + (q^* \, i \mid q^* \, p) - (q^* \, i \mid pq^*) \, . \tag{37}$$

With these results, it is possible to write the effect of the monoexcited configurations in the following form:

$$\begin{aligned}E^{(2)}_{pq^*,1} &= \sum_{i}^{a}{}' \sum_{j^*}^{b}{}' \begin{Bmatrix} [(j^* \, p \mid q^* \, i) - 2(j^* \, p \mid iq^*)]^2 \\ (j^* \, p \mid q^* \, i)^2 \end{Bmatrix} \frac{1}{\varepsilon_{j^*} - \varepsilon_{q^*} - \varepsilon_i + \varepsilon_p} \\ &+ \sum_{i}^{a}{}' \left[\varepsilon_{ip} + \begin{Bmatrix} -(q^* \, i \mid q^* \, p) - 2(q^* \, i \mid pq^*) \\ (q^* \, i \mid q^* \, p) \end{Bmatrix} \right]^2 \frac{1}{\varepsilon_p - \varepsilon_i} \\ &+ \sum_{j^*}^{b}{}' \left[\varepsilon_{j^* q^*} \begin{Bmatrix} (pq^* \mid pj^*) + 2(pq^* \mid j^* \, p) \\ -(pq^* \mid pj^*) \end{Bmatrix} \right]^2 \frac{1}{\varepsilon_{j^*} - \varepsilon_{q^*}} \, .\end{aligned} \tag{38}$$

Here $\varepsilon_{j^* q^*}$ and ε_{ip} are zero if one uses the canonical SCF Molecular Orbitals and the expression of the matrix element between the monoexcited states is unique.

IX. Final Expression of the Second-Order Corrected Transition Energy

We may now bring together the effects of the "tri-, di- and mono-excited" states. Using Eq. (19—20) one gets the final expression of the 2nd order corrected transition energy:

$$\Delta E^{\mathrm{CI}} \simeq \Delta E^{(2)} = \Delta E^{\mathrm{SCF}} +$$

$$+ 2 \sum^{a}{}' \sum_{i<k}{}' \sum_{j^*}^{b}{}' \, [(ik \mid q^* \, j^*)^2 + (ik \mid j^* \, q^*)^2 - (ik \mid q^* \, j^*) \, (ik \mid j^* \, q^*)] \left[\frac{1}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_k} - \frac{1}{\varepsilon_{j^*} + \varepsilon_p - \varepsilon_i - \varepsilon_k} \right]$$

$$
\begin{aligned}
&+2\sum_{i}^{a}{}'\sum_{j^*<l^*}^{b}{}'\sum{}'\left[(ip \mid j^*\,l^*)^2+(ip \mid l^*\,j^*)^2-(ip \mid j^*\,l^*)\,(ip \mid l^*\,j^*)\right]\left[\frac{1}{\varepsilon_{j^*}+\varepsilon_{p^*}-\varepsilon_i-\varepsilon_p}\right.\\
&\qquad\qquad\left.-\frac{1}{\varepsilon_{j^*}+\varepsilon_{l^*}-\varepsilon_i-\varepsilon_{q^*}}\right]+\\
&+\sum_{i<k}^{a}{}'\sum{}'\frac{2(ik \mid q^*\,q^*)^2}{2\varepsilon_{q^*}-\varepsilon_i-\varepsilon_k}-\frac{[(ik \mid pq^*)\pm(ik \mid q^*\,p)]^2}{\varepsilon_{q^*}+\varepsilon_p-\varepsilon_i-\varepsilon_k}+\\
&+\sum_{j^*<l^*}^{b}{}'\sum{}'\frac{2(pp \mid j^*\,l^*)^2}{\varepsilon_{j^*}+\varepsilon_{l^*}-2\varepsilon_p}-\frac{[(q^*\,p \mid j^*\,l^*)\pm(q^*\,p \mid l^*\,j^*)]^2}{\varepsilon_{j^*}+\varepsilon_{l^*}-\varepsilon_p-\varepsilon_{q^*}}+\\
&+\sum_{i}^{a}{}'\sum_{j^*}^{b}{}'(ii \mid q^*\,j^*)^2\left[\frac{1}{\varepsilon_{j^*}+\varepsilon_{q^*}-2\varepsilon_i}-\frac{1}{\varepsilon_{j^*}+\varepsilon_p-2\varepsilon_i}\right]+\\
&+(ip \mid j^*\,j^*)^2\left[\frac{1}{2\varepsilon_{j^*}-\varepsilon_i-\varepsilon_p}-\frac{1}{2\varepsilon_{j^*}-\varepsilon_i-\varepsilon_{q^*}}\right]+\\
&+\left\{\begin{matrix}3(ip \mid j^*\,q^*)^2\\ 4(ip \mid j^*\,q^*)^2+3(ip \mid q^*\,j^*)^2-4(ip \mid j^*\,q^*)\,(ip \mid q^*\,j^*)\end{matrix}\right\}\frac{1}{\varepsilon_{j^*}+\varepsilon_{q^*}-\varepsilon_i-\varepsilon_p}-\\
&-\frac{2}{\varepsilon_{j^*}-\varepsilon_i}\left\{[(iq^* \mid j^*\,q^*)-(ip \mid j^*\,p)]^2+[(ip \mid pj^*)-(iq^* \mid q^*\,j^*)]^2-\right.\\
&\left.-[(ip^* \mid j^*\,q^*)-(ip \mid j^*\,p)]\,[(ip \mid pj^*)-(iq^* \mid q^*\,j^*)]+\left\{\begin{matrix}0\\ 2(ip \mid pj^*)\,(iq^* \mid q^*\,j^*)\end{matrix}\right\}\right\}-\\
&-\frac{1}{\varepsilon_{j^*}-\varepsilon_{q^*}-\varepsilon_i-\varepsilon_p}\left\{\begin{matrix}[(j^*\,p \mid q^*\,i)-2(ip \mid j^*\,q^*)]^2\\ (j^*\,p \mid q^*\,i)^2\end{matrix}\right\}+\\
&+\sum_{i}^{a}{}'\frac{(ii \mid q^*\,q^*)^2}{2\varepsilon_{q^*}-2\varepsilon_i}+\frac{2(ip \mid q^*\,q^*)^2}{2\varepsilon_{q^*}-\varepsilon_i-\varepsilon_p}-\\
&-\frac{1}{\varepsilon_{q^*}+\varepsilon_p-2\varepsilon_i}\left[[(q^*\,i \mid q^*\,q^*)-(pi \mid pq^*)\mp(pi \mid q^*\,p)]^2+\left\{\begin{matrix}2(ii \mid pq^*)^2\\ 0\end{matrix}\right\}\right]-\\
&-\frac{1}{\varepsilon_p-\varepsilon_i}\left[\varepsilon_{ip}+\left\{\begin{matrix}(q^*\,i \mid q^*\,p)-2(q^*\,i \mid pq^*)\\ (q^*\,i \mid q^*\,p)\end{matrix}\right\}\right]^2+\\
&+\sum_{j^*}^{b}{}'\frac{(pp \mid j^*\,j^*)^2}{2\varepsilon_{j^*}-2\varepsilon_p}+\frac{2(pp \mid j^*\,q^*)^2}{\varepsilon_{j^*}+\varepsilon_{q^*}-2\varepsilon_p}-\\
&-\frac{1}{2\varepsilon_{j^*}-\varepsilon_p-\varepsilon_{q^*}}\left[[(pp \mid pj^*)-(q^*\,p \mid q^*\,j^*)\mp(pq^* \mid q^*\,j^*)]^2+\left\{\begin{matrix}2(q^*\,p \mid j^*\,j^*)\\ 0\end{matrix}\right\}\right]-\\
&-\frac{1}{\varepsilon_{j^*}-\varepsilon_{q^*}}\left[\varepsilon_{j^*q^*}+\left\{\begin{matrix}-(pq^* \mid pj^*)+2(pq^* \mid j^*\,p)\\ -(pq^* \mid pj^*)\end{matrix}\right\}\right]^2\\
&+\frac{(pp \mid q^*\,q^*)^2}{2\varepsilon_{q^*}-2\varepsilon_p}-\left\{\begin{matrix}2((pq^* \mid q^*\,q^*)-(pp \mid q^*\,p)\\ 0\end{matrix}\right\}^2\frac{1}{\varepsilon_{q^*}-\varepsilon_p}\,.
\end{aligned}
\tag{39}
$$

This formula looks very complex but it may be translated into very simple operationnal rules which precise what configurations must be taken into account for the calculation of the excitation energy $p \to q^*$:

One must calcule the effect of all the monoexcited states on the desired mono excited state.

The only triexcited configurations to be considered are of the following type:

$$
\begin{array}{c|l}
p & q^* \\
\bar{p} & \bar{q}^* \\
i & j^*\,.
\end{array}
$$

The diexcited configurations where none of the orbitals p and q^* are implied in the excitations, do not play any role in the second order corrected transition energy.

For the diexcited configurations where one of the orbital p or q^* is involved once and only once in the excitations, this effect on the ground state must be divided by a factor 2 in the calculation of the transition energy.

The diexcited configurations where the orbitals p or (or and) q^* are involved at least twice in the excitations appear by their normal action on the ground state and the excited state.

These rules are summarized in the Table.

One may derive an amazing conclusion from these rules. Let us consider the series of linear polyenes. We have shown that the 2nd order correlation energy increases as the number n of carbon atoms in the system. This is due to the $\frac{n^2(n-1)^2}{4}$ terms involved in the summation:

$$4 \underset{i<k}{\sum\sum} \underset{j^*<l^*}{\sum\sum} \frac{(ik \mid j^* l^*)^2 + (ik \mid l^* j^*)^2 - (ik \mid j^* l^*)\,(ik \mid l^* j^*)}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k} .$$

Let us make a closure approximation and write:

$$\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k = 2\Delta E \quad \text{for all } i, k, j^*, l^* .$$

Then one may conclude that $[(ik \mid j^* l^*)^2 + (ik \mid l^* j^*)^2 - (ik \mid j^* l^*)\,(ik \mid l^* j^*)]$ tends to $\frac{2\Delta E\varepsilon}{n(n-1)^2}$ where ε is the correlation energy per electron for the ground state.

Table. *Summary of the configurations needed for the calculation of the transition $p \to q^*$*

Monoexcited	$\Sigma\,\Sigma$ all	Normal action on the excited state
Diexcited	$\Sigma\,\Sigma\,\Sigma \begin{array}{c\|cc\|c} i & j^* & i & q^* \\ p & l^* & k & j^* \end{array}$	Normal action on the excited state; divide by 2 the action on the ground state
	$\begin{array}{c\|cc\|cc\|cc\|c} i & j^* & i & l^* & i & q^* & i & l^* \\ \bar{p} & \bar{l}^* & \bar{p} & \bar{j}^* & \bar{k} & \bar{j}^* & \bar{k} & \bar{q}^* \end{array}$	
	$\Sigma\,\Sigma \begin{array}{c\|cc\|c} i & j^* & i & j^* \\ \bar{i} & \bar{q}^* & \bar{p} & \bar{j}^* \end{array}$	Normal action on the excited state; divide by 2 the action on the ground state
	$\Sigma\,\Sigma \begin{array}{c\|cc\|cc\|c} i & j^* & i & j^* & i & q^* \\ p & q^* & \bar{p} & \bar{q}^* & \bar{p} & \bar{j}^* \end{array}$	Normal action on both the ground and excited states
	$\begin{array}{c\|cc\|c} p & j^* & i & q^* \\ \bar{p} & \bar{l}^* & \bar{k} & \bar{q}^* \end{array}$	
	$\Sigma \begin{array}{c\|cc\|c} p & j^* & i & q^* \\ \bar{p} & \bar{q}^* & \bar{p} & \bar{q}^* \end{array}$	
	$\begin{array}{c\|cc\|c} p & j^* & i & q^* \\ \bar{p} & j^* & \bar{i} & \bar{q}^* \end{array}$	
	$\begin{array}{c\|c} p & q^* \\ \bar{p} & \bar{q}^* \end{array}$	
Triexcited	$\Sigma\,\Sigma \begin{array}{c\|c} p & q^* \\ \bar{p} & \bar{q}^* \\ i & j^* \end{array}$	Normal action on the excited state

Then in the calculation of the transition energy the leading terms are,

$$2 \sum_{i<k}' \sum' \sum_{j^*}' \frac{(ik \mid j^* q^*)^2 + (ik \mid q^* j^*)^2 - (ik \mid j^* q^*)\,(ik \mid q^* j^*)}{2\Delta E} + \\ + 2 \sum_{i}' \sum' \sum_{k^*<l^*}' \frac{(ip \mid j^* l^*)^2 + (ip \mid l^* j^*)^2 - (ip \mid j^* l^*)\,(ip \mid l^* j^*)}{2\Delta E} .$$

Thus we have $2(n-1)^2\,(n-2)$ terms. They finally will give:

$$\delta E \simeq 2\varepsilon \frac{(n-2)}{n} \simeq 2\varepsilon \,. \tag{40}$$

We have then the following *corollary*: the effect of the di- and triexcited configurations on the transition energy in the linear polyenes tends to a constant equal to twice the correlation energy per electron.

(We exclude here the "monoexcited states", the effect of which is non negligible, due to their increasing proximity).

The theorem may be generalized in two directions:

it remains true for the calculation of the difference between the properties of the excited and ground state, provided that this observable is linked to a bielectronic, spin independant, operator;

in a later paper an extension will be given to the calculation of ionization potentials and electroaffinity.

X. Singlet-Triplet Splitting

This formula shows also that the difference between the corresponding singlet et triplet states (if they are both well separated) may be expressed only with a *double* summation:

$$\begin{aligned}
(S-T)_{pq^*} = 2K_{pq^*} & + \\
& + \sum_{i<k}^{a}{}' \sum{}' - \frac{4(ik \mid p\,q^*)\,(ik \mid q^*\,p)}{\varepsilon_{q^*} + \varepsilon_p - \varepsilon_i - \varepsilon_k} + \\
& + \sum_{j^*<l^*}^{b}{}' \sum{}' - \frac{4(q^*\,p \mid j^*\,l^*)\,(q^*\,p \mid l^*\,j^*)}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_p - \varepsilon_{q^*}} + \\
& + \sum_{i}^{a}{}' \sum_{j^*}^{b}{}' + \frac{2(ip \mid p\,j^*)\,(iq^* \mid q^*\,j^*)}{\varepsilon_{j^*} - \varepsilon_i} - \\
& - \frac{(ip \mid j^*\,q^*)^2 + 3(ip \mid q^*\,j^*)^2 - 4(ip \mid j^*\,q^*)\,(ip \mid q^*\,j^*)}{\varepsilon_{j^*} + \varepsilon_{q^*} - \varepsilon_i - \varepsilon_p} + \\
& + \frac{4(ip \mid p\,j^*)\,(iq^* \mid q^*\,j^*)}{\varepsilon_{j^*} - \varepsilon_i} - \\
& - \frac{4(ip \mid j^*\,q^*)^2 - 4(ip \mid j^*\,q^*)\,(j^*\,p \mid q^*\,i)}{\varepsilon_{j^*} - \varepsilon_{q^*} - \varepsilon_i + \varepsilon_p} + \\
& + \sum_{i}^{a}{}' - \frac{2(ii \mid p\,q^*)^2 - (pi \mid q^*\,p)\,[(q^*\,i \mid q^*\,q^*) - (pi \mid pq^*)]}{\varepsilon_{q^*} + \varepsilon_p - 2\varepsilon_i} - \\
& - \frac{4(q^*\,i \mid pq^*)^2 - 4(q^*\,i \mid pq^*)\,[\varepsilon_{ip} + (q^*\,i \mid q^*\,p)]}{\varepsilon_p - \varepsilon_i} + \\
& + \sum_{j^*}^{b}{}' - \frac{2(pq^* \mid j^*\,j^*)^2 - (pq^* \mid q^*\,j^*)^2\,[(pp \mid pj^*) - (q^*\,p \mid q^*\,j^*)]}{2\varepsilon_{j^*} - \varepsilon_p - \varepsilon_{q^*}} - \\
& - \frac{4(pq^* \mid j^*\,p)^2 - 4(pq^* \mid j^*\,p)\,[-\varepsilon_{j^*\,q^*} + (pq^* \mid pj^*)]}{\varepsilon_{j^*} - \varepsilon_{q^*}} - \\
& - \frac{2[(pq^* \mid q^*\,q^*) - (pp \mid q^*\,p)^2]}{\varepsilon_{q^*} - \varepsilon_p} .
\end{aligned} \tag{41}$$

Conclusion

We would like to present four concluding remarks.

The first one concerns the case where the atomic and molecular orbitals belong to different symmetry species (for instance σ and π orbitals in organic conjugated compounds). Then, if we are interested in a transition between orbitals of the same type of symmetry (let us say a $\pi_p \to \pi_q^*$ transition), all the molecular integrals necessary to calculate the transition energy (see Eq. 39) imply at least once the orbital π_q or π_q^*. Then to be different from zero, they must involve two σ orbitals and two π orbitals, or four π orbitals. Thus the calculation of the $\pi - \pi^*$ transition energies only implies the knowledge of $\pi\,\pi$ and $\sigma\,\pi$ integrals: the $\sigma\,\sigma$ integrals are not implied. That remark could help to analyse the disturbing problem of the Pariser-Parr parametrisation of bielectronic integrals and to see in what measure it takes into account correlation effects and in what measure it is introduced to correct implicitly the basis of atomic orbitals.

We started from the ground state Hartree-Fock wave function. This procedure is the most natural but not very symmetrical: one could start as well from the excited self-consistent wave function. The most esthetic way of doing would be to start from a zeroth order wave function which makes stationary the transition energy. This wave function could be got from Nesbet's operator formalism [11] or by the use of an effective Hamiltonian [12]. It is likely that such a procedure would symmetrise the expressions.

Although we have presented our demonstration for a molecular problem with self-consistent zeroth-order wave functions, the cancellation is a more general phenomenon: it occurs also for atomic and other correlation problems. And it is not neccessary for the zeroth order orbitals to be self-consistent.

This paper has been directed towards practical applications. This is the reason why we limited our demonstration to the second order corrections. The demonstration of the cancellation of the quadruple summations is quite easy by itself: but we wanted to derive the final formulas and the selection rules, and this makes the calculations long and delicate. In a further paper we shall demonstrate that similar cancellations of the leading summations occurs at all the orders of the perturbation expansion.

Appendix

A) (Near)-Degeneracy Case

One must distinguish two types of (near)-degeneracy.

a) (near)-degeneracy between monoexcited states differing by one orbital only.

In non symetrical compounds, this case if very frequent for the lowest excited state. In effect, if the lowest excited state corresponds to the transition $n \to n+1$, the nearest excited states correspond to the transition $n \to n+2$ and $n-1 \to \to n+1$.

Let be two monoexcited states only differing by one orbital. For instance:

$$\Psi_{pq^*} = \frac{1}{\sqrt{2}}\left(|\ldots q^*\,\bar{p}\ldots| \pm |\ldots p\bar{q}^*\ldots|\right) \tag{42}$$

and

$$\Psi_{pt^*} = \frac{1}{\sqrt{2}}\left(|\ldots t^*\,\bar{p}\ldots| \pm |\ldots p\bar{t}^*\ldots|\right).$$

If the two "states" interact strongly, the eigenfunctions of the degenerate submatrix are:

$$\begin{aligned} \Phi_1 &= c_1\,\Psi_{pq^*} + c_2\,\Psi_{pt^*} \\ \Phi_2 &= -\,c_2\,\Psi_{pq^*} + c_1\,\Psi_{pt^*} \end{aligned} \tag{43}$$

where c_1 and c_2 are of the same order of magnitude. Then Φ_1 may be written:

$$\Phi_1 = \frac{1}{\sqrt{2}}\left[\left|\ldots(c_1\,q^* + c_2\,t^*)\,\bar{p}\ldots\right| \pm \left|\ldots p(c_1\,\bar{q}^* + c_2\,\bar{t}^*)\ldots\right|\right]. \tag{44}$$

Thus it is sufficient to change the two Molecular Orbitals q^* and t^* according to the transformation:

$$\begin{aligned} q'^* &= c_1\,q^* + c_2\,t^* \\ t'^* &= -\,c_2\,q^* + c_1\,t^*\,. \end{aligned} \tag{45}$$

Now the non-degenerate treatment may be applied: the two states Φ_1 and Φ_2 are well separated, and their zeroth-order wave-function keeps the form of a single determinant.

The conclusions are exactly the same when the two states in strong interaction differ by the ground state occuppied orbital (Ψ_{pq^*} and Ψ_{pq^*}). In these cases the quantities ε_{ip} and $\varepsilon_{j^*q^*}$ in Eqs. (38, 39 and 41) may be different from zero.

b) (near)-degeneracy between states differing by two orbitals

Let us suppose that Ψ_{pq^*} and Ψ_{st^*} are near-degenerate. We may call Ψ_1 and Ψ_2 the eigenfunctions of the submatrix built with Ψ_{pq^*} and Ψ_{st^*}:

$$\begin{aligned} \Psi_1 &= c_1\,\Psi_{pq^*} + c_2\,\Psi_{st^*} \\ \Psi_2 &= -\,c_2\,\Psi_{pq^*} + c_1\,\Psi_{st^*}\,. \end{aligned} \tag{46}$$

Among the triexcited states many interact with Ψ_{pq^*} *or* Ψ_{st^*}, but only:

$$\begin{array}{c|c} p & q^* \\ s & t^* \\ i & j^* \end{array} \quad \begin{array}{c|c} p & q^* \\ \bar{s} & \bar{t}^* \\ \bar{i} & \bar{j}^* \end{array} \quad \begin{array}{c|c} p & q^* \\ i & j^* \\ \bar{s} & \bar{t}^* \end{array} \qquad \text{(and the correct spin permutations)}$$

interact with Ψ_{pq^*} *and* Ψ_{st^*}.

Then in the quadruple sum:

$$\sum_{\substack{i<k \\ \neq p,\,s}} \sum \; \sum_{\substack{j^*<l^* \\ \neq q^*,\,t^*}} \sum \,.$$

One may couple corresponding terms, $\left\langle \Psi_1 \middle| H \middle| \begin{array}{c|c} p & q^* \\ i & j^* \\ k & l^* \end{array} \right\rangle$ and $\left\langle \Psi_1 \middle| H \middle| \begin{array}{c|c} s & t^* \\ i & j^* \\ k & l^* \end{array} \right\rangle$ for instance. The denominators are the same: $\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k$. The matrix elements only differ by a coefficient:

$$\begin{aligned} \left\langle \Psi_1 \middle| H \middle| \begin{array}{c|c} p & q^* \\ i & j^* \\ k & l^* \end{array} \right\rangle &= c_1[(ik \mid j^*\,l^*) - (ik \mid l^*\,j^*)] \\ \left\langle \Psi_1 \middle| H \middle| \begin{array}{c|c} s & t^* \\ i & j^* \\ k & l^* \end{array} \right\rangle &= c_2[(ik \mid j^*\,l^*) - (ik \mid l^*\,j^*)]\,. \end{aligned} \tag{47}$$

Then one meets in the sum:

$$\frac{[(ik \mid j^* l^*) - (ik \mid l^* j^*)^2]}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k} (c_1^2 + c_2^2) = \frac{[(ik \mid j^* l^*) - (ik \mid l^* j^*)]^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k} \,. \tag{48}$$

Thus the cancellation of the quadrupole summations occurs in the same way between $\sum^a \sum_{i<k} \sum^b \sum_{j^*<l^*}$ in $E_0^{(2)}$ and $\sum''^a \sum''_{i<k} \sum''^b \sum''_{j^*<l^*}$ in $E^{(2)}_{pq^*,3}$.

In that case also the second order corrections are expressed with triple summations only.

B) Choice of the Transition Energies Involved in the Denominators of R.S. Expansion

For the sake of simplicity we have considered as zeroth order Hamiltonian, the canonical H.F. Hamiltonian:

$$H^{\mathrm{SCF}} = \sum_i h(i) + \sum [\sum_j^{\mathrm{occ}} 2J_j(i) - K_j(i)] + C \tag{49}$$

where h is the monoelectronic part of H_{exact}, J_j and K_j the usual coulomb and exchange operators. In that model the eigenvalues of the zeroth order Hamiltonian are the sums of the monoelectronic energies summed over the orbitals occuppied in the different configurations.

This choice enables us to use the same transition energies for all the configurations corresponding to a given spacefunction. And this condition was necessary for our demonstration.

Most of the second order calculations were made in this scheme (7, 5, 12). NESBET [2] however had used a different approximation. He used for $E_o - E_i$, what is generally considered to be the true SCF transition energie: $E_o - E_i = \langle o \mid H \mid o \rangle - \langle i \mid H \mid i \rangle$. So did KELLY [6] from more complex considerations. We have discussed in a previous paper these two approximations [8]. We have shown that the zeroth-order hamiltonian is then

where
$$H'^0 = H^{\mathrm{SCF}} + \sum_i \langle i \mid V \mid i \rangle \mid i \rangle \langle i \mid \tag{50}$$

where $V = H - H^{\mathrm{SCF}}$. We proposed to call Epstein-Nesbet expansion this variant of the Rayleigh Schrödinger expansion, first proposed by P. S. EPSTEIN [4]. We have shown that the second-order correction is more important, and the third order correction smaller when one uses H'^0, as unperturbed Hamiltonian. The gain may be important (about 30%), at least for π problems. STEINER [14] discussed others partitions of the exact Hamiltonian.

In another paper [3] we applied the two expansions to the π electrons problem, in the series of linear polyenes.

The superiority of Epstein-Nesbet partition is linked to the importance of the first order correlation correction for the excited states: for the monoexcited states $\langle ij^* \mid V \mid ij^* \rangle = J_{ij^*}$, $J_{ij^*} - 2K_{ij^*}$ is often of the same order of magnitude than the observed transition energies. We cannot use the pure Epstein-Nesbet procedure here, since it distinguishes between the energies of the different configurations or S^2 eigenfunctions corresponding to a given space function. But we may very well improve our results by taking for all these configurations or S^2 eigenfunctions the same transition energies, equal for instance to the transition energy of one of them. Doing so we only let on the diagonal of the perturbation matrix small terms $\langle i \mid V' \mid i\rangle \ll \langle i \mid V \mid i\rangle$. We used for instance as transition energies of the diexcited configurations $\begin{array}{c|c} i & j^* \\ k & l^* \end{array}$.

$$\begin{aligned} E_0 - E\begin{smallmatrix} i \\ k \end{smallmatrix}\Big|\begin{smallmatrix} j^* \\ l^* \end{smallmatrix} &= \tfrac{1}{2}\,(E_0 - E_{ij^*} + E_0 - E_{il^*} + E_0 - E_{kj^*} + E_0 - E_{kl^*}) \\ &= \varepsilon_i + \varepsilon_k - \varepsilon_{j^*} - \varepsilon_{l^*} + \tfrac{1}{2}\,[(J_{ij^*} - K_{ij^*}) + (J_{il^*} - K_{il^*}) + \\ &\quad + (J_{kj^*} - K_{kj^*}) + (J_{kl^*} - K_{kl^*})]\,. \end{aligned} \tag{51}$$

This approximation is very convenient since all the transitions of p excited states are calculated from the transition energies of the monoexcited states. We verified that in the series of linear polyenes the difference with the result of the Epstein-Nesbet expansion for the second order correlation energy ground state is less than 0.02 eV.

Our demonstration is entirely valid with such a definition of the unperturbed Hamiltonian, which combines the speed of the convergency and the formal simplicity, if we add the condition $E_{pq^*} - E\begin{smallmatrix} p \\ i \\ k \end{smallmatrix}\Bigg|\begin{smallmatrix} q^* \\ j^* \\ l^* \end{smallmatrix} = E_0 - E\begin{smallmatrix} i \\ k \end{smallmatrix}\Big|\begin{smallmatrix} d^* \\ l^* \end{smallmatrix}$.

Addendum. J. ČIZEK (private communication concerning unpublished results) has recently demonstrated the cancellation of quadruple summations in the direct expression of the transition energies. His demonstration is based on TOLMATCHEV's unpublished theorems. This completly different demonstration uses the formalism of the Green's functions and Goldstone's diagrams.

Bibliography

1. BRUECKNER, K. A.: In "The Many Body Problem", Les Houches 1958, New York: Wiley 1959.
2. CLAVERIE, P., S. DINER, and J. P. MALRIEU: Internat. J. Quantum Chem. (In press).
3. DINER, S., J. P. MALRIEU and P. CLAVERIE: Theoret. chim. Acta. **8**, 390 (1967)
4. EPSTEIN, P. S.: Physic. Rev. **28**, 695 (1926).
5. GRIMALDI, F.: J. Chem. Physics **43**, 59 (1965).
6. KELLY, H. P.: Physic. Rev. **136**, B, 896 (1964).
7. KIRGNITZ, D. A.: Optika i Spectr. **5**, 485 (1958).
8. LEVY, B.: To be published.
9. MØLLER, C., and M. S. PLESSET: Physic. Rev. **46**, 618 (1934).
10. NESBET, R. K.: Proc. Roy. Soc. A **230**, 312, 922 (1955).
11. – J. Math. Physics **6**, 621 (1965).
12. POLAK, R., and J. PALDUS: Theoret. chim. Acta **5**, 422 (1966).
13. PORTER, C. E., and N. ROSENZWEIG: Annales Academiae Sc. Fennicae, Series A **44**, 4 (1960).
14. STEINER, E.: J. Chem. Physics **46**, 1717 (1967).

Dr. J. P. MALRIEU
Laboratoire de Chimie Quantique
Institut de Biologie Physico-Chimique
13, rue Pierre Curie
Paris 5ème, France