Commentationes

Localized Bond Orbitals and the Correlation Problem

I. The Perturbation Calculation of the Ground State Energy

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A method is proposed to go beyond the SCF result in the calculation of the ground state energies without any variational procedure. One chooses a set of reasonable bonding and antibonding orbitals localized on the chemical bonds. The bonding orbitals are used to built a fully localized determinant. The basis of excited states is built using the antibonding orbitals. One calculates the lower eigenvalue of the CI matrix in this basis by a Rayleigh-Schrödinger expansion. The conceptual and practical advantages of the method are discussed, and the perturbation series is specified in order to satisfy the linked cluster theorem conditions and to retain the advantages of the Epstein-Nesbet partition of the Hamiltonian.

Es wird eine Methode angegeben, die die SCF-Resultate in der Berechnung der Grundzustands-energien übertrifft, ohne die Mittel der Variationsrechnung anzuwenden. Als Basisfunktionen wählt man einen Satz geeigneter bindender and antibindender Orbitale, die auf den chemischen Bindungen lokalisiert sind. Die bindenden Orbitale werden zum Aufbau einer völlig lokalisierten Determinante benutzt. Als Basisfunktionen für die angeregten Zustände benutzt man auch antibindende Orbitale. Man berechnet den tieferen Eigenwert der CI Matrix mit dieser Basis durch eine Rayleigh-Schrödinger-Entwicklung. Die begrifflichen und praktischen Vorteile dieser Methode werden diskutiert. Indem man die Störungsreihe so wählt, daß das "linked cluster"-Theorem erfüllt ist, bleiben die Vorteile der Epstein-Nesbet-Aufspaltung des Hamiltonoperators erhalten.

On propose une méthode pour dépasser la valeur SCF dans le calcul de l'énergie de l'état fonda-mental en évitant tout procédé variationnel. On choisit un jeu raisonnable d'orbitales liantes et anti-liantes sur les liaisons chimiques. Le déterminant totalement localisé est bâti à l'aide des orbitales liantes. Les orbitales antiliantes servent à construire les états excités, base de la matrice d'Interaction de Configuration. La plus basse valeur propre de celle-ci est développée par perturbation. Les avantages conceptuels et pratiques de la méthode sont discutés. On précise une série de perturbation qui permet de combiner les avantages du théorème du linked cluster et de la partition Epstein-Nesbet de l'Hamil-tonien.

1. Introduction

The Chemical Formula as a Zeroth Order Approximation

It is well known that bond additivity is a useful first approximation for the evaluation of many observables (dipole moments, heats of formation, etc.). A natural way to improve this empirical model was to take into account bond-interactions and long time ago Platt [1] proposed empirical systematics to do so. K. Ito [2] improved this model and got a very nice agreement with experimental heats of formation and differences in energies of isomers of many saturated hydro-carbons [3]. These approaches are not frequently used now, and most people

seem to prefer the better standing of quantum mechanical methods, even when fully parametrized and with poor reliability.

Theory, however, has legitimized these empirical systematics. Early theoretical representations of polyatomic molecules in the LCAO-SCF scheme ignored the concept of the chemical bond. Lennard-Jones and Hall [4] demonstrated that one may extract bonds from the molecular SCF wave function, and empirical applications by Hall [5], Brown [6] and Dewar and Pettit [7] gave a justification of the systematics of bond and bond interaction energies.

But these works were derived in the single-determinant approximation and in general in the framework of the Hartree-Fock method. The criteria proposed later by Boys [8], Edmiston and Ruedenberg [9], Magnasco and Perico [10] were used to transform the canonical molecular orbitals into localized molecular orbitals, keeping the SCF determinant invariant. Quantum chemistry generally went back to the chemical bond through the Hartree Fock approximation and it had only a conceptual interest.

Today the SCF wave function is no longer the unique goal and it becomes a step in processes which try to go further towards the exact energy and the exact wave function. To do so one may use variational or perturbational procedures. In correlation problems it is well known now that the use of localized virtual orbitals improves the result of the various approximations proposed to calculate the correlation energy. This had been suggested by Sinanoğlu [11] and Nesbet [12]. From the "early" work of Watson [13] it has been verified many times for atoms that it was worthwile to localize the virtual orbitals in that region where the occupied orbitals have a high density. The same need occurs in small molecules [14, 15]. In large molecules, when one calculates the correlation energy with the minimal basis set, the virtual and occupied orbitals are already defined in the same region. But the relocalization of the occupied orbitals on bonding bond orbitals, and of the virtual orbitals on antibonding orbitals defined on the same bonds, increases the interactions of the ground state with the doubly excited states and provides a better result in the pair APSG method [16] and a better second order correlation energy [17].

Under these conditions the question becomes: is it really necessary to go through the SCF procedure? Instead of making a long variational calculation and then a long localization procedure starting from a zeroth order wave-function which is close to the chemical formula, why should one not start from a wave function built with molecular orbitals fully localized on the chemical bonds (FLBO)? Can we not consider the chemical formula as a reasonable zeroth order approximation?

There have been some attempts in atomic problems to avoid the SCF step. Such are the Z expansion [18] and recent works by Goodisman [19] and Musher [20]. Tolmatchev even started from hydrogenoid orbitals without any screening effect [21]. When the starting point is good enough the process seems to converge. In our problem the delocalization is not very important. In conjugated and aromatic systems, various criteria give strongly localized pairs of electrons from the SCF orbitals (98 % in linear polyenes, 88 % in benzene, 90 % in naphtalene) [22]. In σ systems calculated with the CNDO approximation the delocalization does not exceed 1 or 2 % [17]. Thus a fully localized determinant representing the

chemical formula could have a large overlap with the SCF one and the delocalization energy (difference between the fully localized determinant and the SCF wave function) could be of the same order of magnitude than the correlation energy. These facts have been proved by *ab initio* calculations on NH_3 and on other small polyatomic molecules [23–25].

Then, the question is to improve this wave function. The first idea may be to use the single particle approximation to improve the localized molecular orbitals, as in the old empirical LCBO systematics [5–7], by taking into account their interactions: Hamano perturbed the bond orbitals [26], but this wave function does not bypass the SCF result. To do this, one needs a multiconfigurational wave function. This may be done by the various pair-approximations [27], for instance the Parr and Parks version [28], but this technique lacks the effects of delocalization and the interbond correlation and does not give very good results [23]. The other possibility is to perform the classical configuration interaction, but the dimension of the CI matrix becomes prohibitive rapidly. One is compelled to truncate the number of MO's used [23] or the basis of configurations [24].

In fact, the perturbation technique indicates a rational way to truncate CI matrices [29] and enables one to get rapidly reasonable estimates of the exact energy in the corresponding basis set.

The procedure we propose may be decomposed into four steps:

1. One builds a set of reasonable bond orbitals, both bonding and antibonding.

2. One uses the bonding orbitals to construct a fully localized determinant. This determinant will be the zeroth order wave function.

3. One uses the antibonding orbitals to build excited states (mono-, di-excited states). The CI matrix is considered to be constructed on such a basis of configurations.

4. One develops the lowest eigenvalue and eigenstate by a Rayleigh-Schrödinger perturbation expansion.

We want to show that the combined use of localized molecular orbitals and a perturbation development of the CI matrix leads to special advantages:

Each step of the process and each type of terms in the series of the ground state energy has a clear physico-chemical interpretation in terms of bond interaction. This has been pointed out long time ago by Sinanoğlu [30, 31] concerning the bond and lone pair correlation energies, and the intramolecular Van der Waals interactions. The changes in the Hartree-Fock potential (and therefore in the SCF localized MO's) are responsible for slight changes in the intra-bond and inter-bond correlation energies when one goes from one molecule to another. Our fully localized orbitals should be less dependant on the environment and the transferability of our contributions should be improved.

The integrals involving localized orbitals are of different orders of magnitude according to their nature and introduce possible supplementary simplifications at each order of the perturbation expansion.

The purpose of this paper is to present the framework of the method and to give some details about the perturbation series and techniques used hereafter.

The second paper of the series gives algebraic and numerical applications to π conjugated systems. We show the relations between the perturbation expansion (and the related Goldstone's diagrams) and the chemical graph (i.e.

the molecular topology). Comparison is made with the full CI in the same basis set, to study the convergence process.

The third paper is devoted to sigma systems, using the CNDO approximations of the integrals. The general formulae are given together with numerical applications.

The fourth paper studies the stability of the method with respect to the choice of the bond orbitals: the role of hybridization and of bond polarity on energies at different orders is investigated.

In a fifth paper the density matrix at different orders is analyzed, and mono-electronic observables are calculated.

2. Description of the Method

A. Choice of the Bond Orbitals and of the Zeroth Order Determinant. One uses molecular orbitals which are defined on the chemical bonds. For instance, if we work in a minimal basis set, we may define one bonding and one antibonding orbital for each chemical bond. If we consider the ethylene molecule for instance, one may define 4 CH bonding and 4 CH antibonding orbitals, 1 C–C σ and 1 C–C π bonding orbitals and their corresponding antibonding orbitals. If one includes the 1s orbitals in the basis set, they may become innershell lone pairs. For the formaldehyde molecule in the minimal basis set one also defines two lone-pairs among the valence electrons on the oxygen-molecule. In the minimal basis set no antibonding orbital corresponds to the lone pairs. If we use an extended basis set, for instance $3p_z$ atomic orbitals in the ethylene molecule, we may use them to define two unoccupied orbitals – one symmetrical and one antisymmetrical –, or two unoccupied lone-pairs. The use of an extended basis set does not present any difficulty within the framework of this method.

The bond molecular orbitals may be more or less refined. One may build them with special diatomic wave functions [32] or simply by a proper combination of two atomic (hybrid) orbitals. For instance the C–C σ bond orbitals in ethylene may be represented with two atomic canonical sp^2 hybrids with equal weights, or with optimized hybrids [25]. The main problem concerns the orthogonality of the basis set. The fully localized bond orbitals are not orthogonal in general. If one applies for instance a $S^{-1/2}$ orthogonalization procedure, they become delocalized in a way which depends on the molecule. The orthogonal bond orbitals depend on the geometry and the environment and have "tails" over the whole framework of the molecule. For π systems however, Fisher Hjalmars [33] proved that one could define quasi orthogonal atomic orbitals which lead to the so-called Pariser-Parr-Pople approximations of integrals. Such approximations have been accepted as valid for σ orbitals and are used in the CNDO hypothesis. In fact the σ *atomic* orbitals are very far from orthogonality ($S \cong 0.6$), but the overlap between fully localized *bond* orbitals never exceeds 0,2, and the σ bond orbitals may be considered to be as orthogonal as the π atomic orbitals. This approximation should be much better than the very crude CNDO hypothesis, since it does not suppose the neglect of the overlap *in* the chemical bond. Later applications [34]

will be devoted to the cases where overlap between bond orbitals is taken into account, but we shall mainly consider the case where Pariser-Parr type approximations are valid.

For aromatic systems like benzene, the choice of the bond orbitals is arbitrary: one may choose for instance one Kékuléan formula or the other. Both will lead to the same development. In naphtalene one may built different types of kékuléan like formulas, which are not equivalent. The symmetry conditions sometimes favour one of these graphs, but it is not always possible to satisfy them (cf. the anthracene molecule). The criterion for the choice of the zeroth order fully localized wave function is its energy and one may analyse the convergence of the process by comparing the results obtained from different reasonable zeroth order wave functions. This degree of freedom does not exist for σ systems.

For σ systems there is a degree of freedom in the choice of the hybrids which are used to built the bond orbitals. For open chain molecules and unstrained cycles the classical sp^2 or sp^3 hybridization state may be used. The question becomes more important for strained molecules and a certain research for the best hybridization becomes necessary. The influence of the hybridization on the process will be studied in paper IV. For conjugated systems one may consider to use two sets of orbitals to represent the double bonds: a pair of equivalent C–C bonds or a π and a σ bond. The results apparently favour the classical $\sigma - \pi$ representation [34].

For heteroatomic systems one must also choose the polarity of the bond orbitals. The relative accuracy of the vector model of bond dipole moments to construct the molecular dipole moment, indicates that the polarity of a given bond is mainly determined by the nature of the two atoms, and that the other bonds only slightly perturb the electronic distribution in the bond. This is also confirmed by the content and the success of Del Re's picture [35]. Thus we propose to determine a canonical polarity for each type of bond from calculations on small systems or bond dipole moments, and use it as a basic parameter each time we meet this type of bond: Then the bonding and antibonding orbitals on bond i may be represented with two hybrids i_1 and i_2 by the linear combination

$$i = \alpha i_1 + \beta i_2 ,$$

$$i^* = \beta' i_1 - \alpha' i_2 ,$$

where α, β, β', α' satisfy the orthonormality conditions and determine the polarity.

When one has choosen the bond orbitals, here supposed to be orthogonal, one builds the zeroth order determinant with the n bonding orbitals.

$$\Phi_0 = \frac{1}{\sqrt{2n!}} |1\,\bar{1}\ldots i\bar{i}\ldots n\bar{n}| .$$

The energy of this determinant is simply calculated as the mean value of the Hamiltonian.

B. *Configuration Interaction.* Then we may built mono excited configurations by "promoting one electron" from the bond orbital i to the antibonding orbital

j^* or diexcited configurations from orbitals i and k to the antibonding orbitals j^* and l^*.

$$\Phi\left(\frac{\bar{j}^*}{\bar{i}}\right) = \frac{1}{\sqrt{2n!}}\,|1\,\bar{1}\ldots i\bar{j}^*\ldots n\bar{n}|\,,$$

$$\Phi\left(\frac{\bar{j}^*\,\bar{l}^*}{\bar{i}\,\bar{k}}\right) = \frac{1}{\sqrt{2n!}}\,|1\,\bar{1}\ldots i\bar{j}^*\ldots k\bar{l}^*\ldots n\bar{n}|\,.$$

Tri, quadri excited states and so on may be constructed in this way, all being orthogonal. Only mono- and diexcited states interact with Φ_0 since the total Hamiltonian H is only bielectronic. If Φ_0 represents a satisfactory representation of the wave function, one may write, using Rayleigh Schrödinger perturbation theory:

$$\Psi_0 \cong \Phi_0 + \sum_{i,j^*} \frac{\left\langle \Phi_0|H|\Phi\left(\dfrac{j^*}{i}\right)\right\rangle}{E_0 - E\left(\dfrac{j^*}{i}\right)}\,\Phi\left(\frac{j^*}{i}\right) + \sum_{ikj^*l^*} \frac{\left\langle \Phi_0|H|\Phi\left(\dfrac{j^*\ l^*}{i\ k}\right)\right\rangle}{E_0 - E\left(\dfrac{j^*\ l^*}{i\ k}\right)}\,\Phi\left(\frac{j^*\ l^*}{i\ k}\right),$$

$$E \cong \langle \Phi_0|H|\Phi_0\rangle + \sum_{ij^*} \frac{\left\langle \Phi_0|H|\Phi\left(\dfrac{j^*}{i}\right)\right\rangle^2}{E_0 - E\left(\dfrac{j^*}{i}\right)} + \sum_{ikj^*l^*} \frac{\left\langle \Phi_0|H|\Phi\left(\dfrac{j^*\ l^*}{i\ k}\right)\right\rangle^2}{E_0 - E\left(\dfrac{j^*\ l^*}{i\ k}\right)}$$

(for the definition of the unperturbed and perturbation Hamiltonians, see § 3, 3). These formulae are always valid if Φ_0 is a good starting point, and the MO's may be delocalized. If the ground state is a SCF determinant, the monoexcited states have zero matrix elements with Φ_0.

We would like to recall here the simple physical significance of each term and some simplifications introduced by the localization:

The interaction with $\Phi\left(\dfrac{i^*}{i}\right)$ introduces a change of the polarity of the bond, under the influence of the environment. These states are the polarization states and give rise to the polarization energy.

The interaction with $\Phi\left(\dfrac{j^*}{i}\right)$ delocalizes the electrons from bond i to the region of bond j. They may be called the delocalization or charge transfer states. The difference between the amount of $\Phi\left(\dfrac{j^*}{i}\right)$ and $\Phi\left(\dfrac{i^*}{j}\right)$ in the wave function gives the charge migrations in the molecule from bond to bond.

The wave function limited to the monoexcited states

$$\Phi = \Phi_0 + \sum_{ij^*} \frac{\left\langle \Phi\left(\dfrac{j^*}{i}\right)|H|\Phi_0\right\rangle}{E_0 - E\left(\dfrac{j^*}{i}\right)}\,\Phi\left(\frac{j^*}{i}\right)$$

should in principle differ only by second order terms from the molecular SCF wave function.

C. Simplifications Introduced by the Use of Bond Orbitals. The diexcited states will enable the perturbed wave function to bypass the SCF determinant and introduce a part of the so-called "correlation energy". One may distinguish several terms in it, according to their order of magnitude and physical significance. The excitation may involve one bond only $\left(\text{excitation} \left(\dfrac{i^* \bar{i}^*}{i \ \bar{i}} \right) \right)$. This leads to the matrix element

$$\left\langle \Phi_0 |H| \Phi \left(\frac{i^* \bar{i}^*}{i \ \bar{i}} \right) \right\rangle = \left\langle i\bar{i} \left| \frac{1}{r_{12}} \right| i^* \bar{i}^* \right\rangle = K_{ii*} = (ii | i^* i^*).$$

This integral may be important (several eV) and is responsible for most of the intra bond correlation energy [30, 17].

The excitation may involve two different bonds, i and j. Let us consider first the excitation $\left(\dfrac{i^* j^*}{i \ j} \right)$. The integral is given by

$$\left\langle \Phi_0 |H| \Phi \left(\frac{i^* j^*}{i \ j} \right) \right\rangle = \left\langle ij \left| \frac{1}{r_{12}} \right| (1 - P) i^* j^* \right\rangle$$

$$= (ij | i^* j^*) \quad \text{if } i \text{ and } j \text{ have different spins}$$

$$= (ij | i^* j^*) - (ij | j^* i^*) \quad \text{if } i \text{ and } j \text{ have the same spin}.$$

$(ij | i^* j^*)$ represents the interaction between the dipolar distribution ii^* and the dipolar distribution jj^*. It decreases as r^{-3} when the distance r between bonds i and j increases and gives raise to most of the interbond dispersion energy or interbond correlation energy [30, 17].

On the contrary, the exchange integral $(ij | j^* i^*)$ represents the interaction between the distributions ij^* and i^*j. These distributions have very small amplitudes if the overlap between the bond orbitals i and j is small. The integral may be considered of order S^2 if one evaluates it by the Mulliken approximation. It is zero if one supposes the ZDO between the bond orbitals. If we consider the excited state $\left(\dfrac{i^* j^*}{i \ i} \right)$ for instance, the integral $(ii | i^* j^*)$ may be expressed by $0.5 \, S_{ij*} [(ij^* | i^* j^*) + (ii | i^* i^*)]$. It is of order S compared with $(ii | i^* i^*)$. If the bond orbitals are supposed to have zero differential overlap (or defined on separate domains) this integral is zero. In general only the integrals $(ij | k^* j^*)$ lead to integrals of order 1 in S. All the other integrals implied in the second order energy $(ij | k^* l^*)$ lead to integrals of order 2 in S. *If one uses the* ZDO *approximation between bond orbitals, the* n^4 *integrals* $(ij | k^* l^*)$ *are zero, and only* n^2 *integrals* $(ij | i^* j^*)$ *are different from zero:* the use of localized orbitals leads to an enormous reduction of the number of non zero integrals. If one does not neglect the overlap between the bond orbitals one has a serious criterion to truncate the basis set according to the S power of the integrals involved. Using the perturbation technique one may use different approximations at the different orders of the perturbation expansion and may, for instance, consider all the integrals to the order of S^2 in the 2nd order energy correction, only the integrals in S^1 in the third order correction, and the few S^0 integrals in the fourth order energy correction.

Thus, the use of bond orbitals enables one to make a rational series of approximations according to the order of magnitude of the integrals. If one assumes the ZDO between bond orbitals, there is an enormous decrease in the number of integrals and one may go further in the perturbation calculation of the ground state energy than one could do using SCF orbitals. Moreover, at each order in the perturbation expansion, the energy correction may be decomposed in different contributions, each of them having a clear physical significance.

As to the computation time one may recall that in the ZDO approximation each SCF process iteration requires the calculation of n^2 elements J_{ij} each of them requiring a calculation over n^2 elements g_{pq}. The computation time increases as n^3. The second order energy calculation requires the calculation of n^4 matrix elements $(ij \mid k^* l^*)$, each of them being computed by a double summation. However this step may be reduced from n^6 to n^5 [36].

In our procedure each element J_{ij} only requires a summation over four orbitals: the computation time of each J_{ij} does not increase with the dimension. The calculation of the zeroth order energy only increases as n^2, as does the calculation of the 2nd order energy since it only requires the calculation of $(ij \mid i^* j^*)$ and $\left(i \left| -\dfrac{V^2}{2} + h \right| j^* \right)$. The calculation of the 3rd order correction needs a time proportional to n^3 and so on: for large systems one obtains a much better energy than the SCF one, in a much shorter time.

3. Perturbation Technique

1. Diagramatic Representation

A. Usual Conventions Concerning Diagrams. Following Feynman's [37] original treatment, different diagramatic representations of perturbation expansion terms are used. For the many body problem in the time independent formalism three kinds of diagrams are well known: Brueckner diagrams [38], Goldstone diagrams [39] and Hugenholtz diagrams [40]. We are going to use Goldstone's formalism just as a mnemomic and visualizing device. Let us recall briefly the principles of diagramatic representation since most quantum chemists are not familiar with them:

a) A matrix element in a basis of mono- or bi-particle functions can be formally said to represent a transition of one or two particles from initial to final states, taking place under the influence of the operator.

Contrary to the usual convention (which is the normal one when the second quantization formalism is used) we consider that initial states are on the left side of the matrix element in the Dirac notation.

b) These virtual transitions are represented by points, one for each particle, which are the nodes of the diagram.

c) The interaction, due to the operator, is represented by a horizontal dotted line originating from one node or joining two nodes, according to the mono or bielectronic character of the operator. In the monoelectronic case, we put a cross to end the dotted line, in order to distinguish these diagrams from similar diagrams defined in § B.

d) At each node there are two vertical oriented and labelled full lines.

e) We orientate the lines as follows: an upward line represents the propagation of a particle in a virtual orbital, a downward line represents the propagation of a particle in a ground state occupied orbital.

f) At a node the particle in the initial state is destroyed and the particle in the final state is created. Destruction and creation correspond to lines coming *to* or *from* the node[1].

g) Indexes at the same place on both sides of the operator (in the matrix element) correspond to the same node: for example, in $\langle ij|v|kl\rangle$ (see Fig. 1), i (destroyed) and k (created) correspond to the first node, and similarly j (destroyed) and l (created) correspond to the second node. These principles are illustrated in Fig. 1.
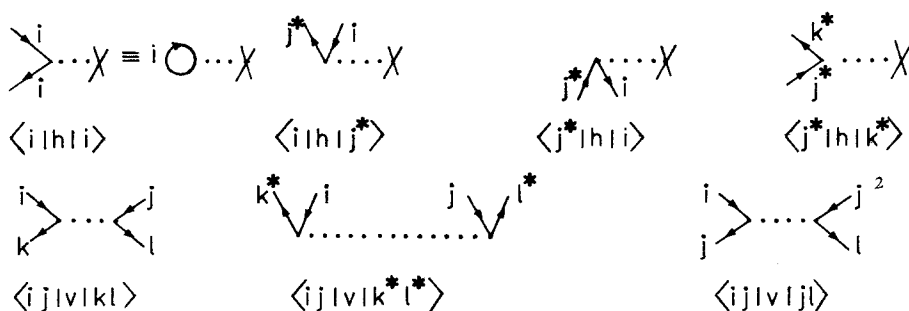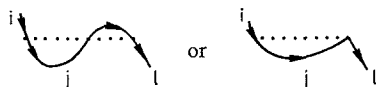

Fig. 1. Graphical representation of matrix elements

To visualize the sequences of interactions that occur in perturbation theory, giving rise to clusters of matrix elements, one represents diagramatically in a vertical order each matrix element after the other from left to right in the formula. A diagram corresponding to such a cluster has only closed propagation lines, since the system must come back to the unperturbed state after all the virtual transitions have taken place. The denominator of the corresponding term of the perturbation series is the product of the energy differences between the unperturbed state and each of the excited states got between two successive interaction lines. Fig. 2 give some typical examples.

A linked diagram (corresponding to a linked cluster) is a diagram in which one may go from any node to any other following interaction and propagation lines. Unlinked diagrams can be drawn as separate parts. In Fig. 2b we have an unlinked fourth order diagram.

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[1] We must remark that these principles which lead to diagrams like those defined in Goldstone's work do not imply a true hole-particle formalism: we destroy a particle in an occupied state and do not create a hole in our diagrams. Goldstone's original formulation suffers from this contradiction which is only a real problem in the second quantization formalism.

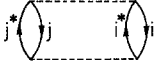[2] This "exchange diagram" is usually drawn as:

which is misleading if one tries to interpret it directly according to the above rules.
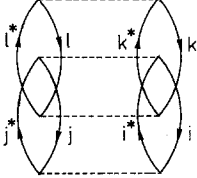
The sign of the final contribution of a given diagram is given by the rule $(-1)^{h+l}$ where h is the number of hole (downwards) propagation lines, and l the number of loops of the diagram.

B. *Correspondance of Diagrams with the Rayleigh-Schrödinger Expansion.* For our present purpose, it is more convenient to use the ordinary form of the Rayleigh-Schrödinger perturbation expansion. The nth order correction to the energy involves a general sum which is built using products of n matrix elements between configurations:

$$\sideset{}{'}\sum_I \sideset{}{'}\sum_J \sideset{}{'}\sum_M \frac{\langle \Phi_0|V|\Phi_I \rangle \langle \Phi_I|V|\Phi_J \rangle \cdots \langle \Phi_M|V|\Phi_0 \rangle}{(E_0 - E_I)(E_0 - E_J)\ldots(E_0 - E_M)},$$

where Σ' means that Φ_0 is excluded from the summation and special terms each of them involving corrections of lower orders to energy and the wave function

a)

$$\frac{(ij \mid i^*j^*)(j^*i^* \mid ji)}{E_0 - E\left(\dfrac{i^*j^*}{ij}\right)}.$$

b)

$$\frac{(ij \mid i^*j^*)(kl \mid k^*l^*)(j^*i^* \mid ji)(l^*k^* \mid kl)}{\left[E_0 - E\left(\dfrac{i^*j^*}{ij}\right)\right]\left[E_0 - E\left(\dfrac{i^*j^*k^*l^*}{ijkl}\right)\right]\left[E_0 - E\left(\dfrac{i^*j^*}{ij}\right)\right]}.$$
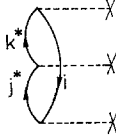
c)

$$\frac{\langle i|h|j^* \rangle \langle j^*|h|k^* \rangle \langle k^*|h|i \rangle}{\left[E_0 - E\left(\dfrac{j^*}{i}\right)\right]\left[E_0 - E\left(\dfrac{k^*}{i}\right)\right]}.$$

Fig. 2. Graphical representation of typical perturbation terms

(Dupont-Bourdelet [41], Messiah [24]). Each term of these sums may be represented by a diagram analogous to (but not identical with) the Goldstone diagrams just described. Each interaction line corresponds to the transition of a configuration to the following one; since two consecutive configurations may differ by one or two spin orbitals, we put one node or two nodes respectively, on the interaction line. The labelling conventions for the full lines are the same as previously. Therefore the new diagrams (hereafter designed as Rayleigh-Schrödinger diagrams, or more briefly RS diagrams) differ graphically from the Goldstone ones by the fact that there may be neither a loop nor a cross on an interaction line. Now V is the sum of a monoelectronic part $\sum_i h(i)$ and of a bielectronic part $\sum_{i,j} V(i,j)$, so that every matrix element $\langle \Phi_K|V|\Phi_L \rangle$ is generally the sum of monoelectronic and bielectronic integrals, and the whole numerator appears therefore as a sum of products of mono- or bielectronic integrals and, dividing by the denominator, the whole Rayleigh-Schrödinger term appears as a sum of terms which correspond exactly to the Goldstone diagrams. Therefore, generally

speaking, each of the RS diagrams we have introduced corresponds to a sum of Goldstone diagrams.

If Φ_K and Φ_L differ by two spin orbitals, $\langle \Phi_K | V | \Phi_L \rangle$ reduces to one bielectronic coulomb integral and, eventually, an exchange integral. Since the exchange integrals are zero in our case (ZDO assumptions), we are left with the coulomb integral; this shows that an interaction line with two nodes in the RS diagram gives an identical interaction line in all corresponding Goldstone diagrams.

Now, if Φ_K and Φ_L differ by one spin orbital (this case is represented by an interaction line with a single node), then

$$\langle \Phi_K | V | \Phi_L \rangle = \langle i_K | h | i_L \rangle + \sum_{m \in \Phi_K, \Phi_L} \langle i_K m | v_e | i_L m \rangle ,$$

where $v_{e(1,2)} = V_{(1,2)} (1 - P_{12})$ in order to include exchange.

Therefore, an interaction line with a single node corresponds to a sum of Goldstone diagrams, one with a cross on the interaction line and the others with two nodes on it.

Due to the ZDO assumptions and the use of localized orbitals, if i_K and i_L do not belong to the same bond (for example $i_K = i$, $i_L = j^*$), all bielectronic integrals in the above formula are zero, so that the correspondance between the two kinds of diagrams becomes very simple in this case: it is sufficient to put a cross on the interaction line of an RS diagram with a single node in order to obtain the unique non zero Goldstone diagram.

On the other hand, if i_K and i_L belong to the same bond (for example $i_K = k$, $i_L = k^*$), then both monoelectronic and bielectronic parts are non zero. This is the only case (in our problem) in which an RS diagram represents a sum of more than one Goldstone diagrams.

Moreover, we shall suppose here and in the applications on alternant hydrocarbons that the bond orbitals have a correct polarity i.e. $\left\langle 0 | V | \left(\dfrac{k^*}{k} \right) \right\rangle = 0$ so that the case under consideration cannot occur for the first and last interaction lines. At the 3$^{\text{rd}}$ order, it is also impossible to have this case for the second line (due to our assumptions, which imply that only the diexcited states $\left(\dfrac{i^* j^*}{ij} \right)$ interact with the ground state configuration). At the 4$^{\text{th}}$ order, this may happen at the second and third lines.

The use of the correspondance between RS and Goldstone diagrams is necessary because the sign rule (cf. end of § A) and the linked cluster theorem (cf. next section 3°) apply to the second ones only. In the large majority of cases there is no single excitation $\left(\dfrac{k^*}{k} \right)$ on lines 2 and 3 and the sign rule and linked cluster selection are directly valid on the RS graphs. In the few cases in which the single excitation or diexcitation $\left(\dfrac{k^*}{k} \right)$ occurs on the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ line, one must decompose the RS diagram in its Goldstone components; if the RS diagram is linked, all its Goldstone components are linked, but the opposite is not true: an unlinked RS diagram involving a single excitation $\left(\dfrac{k^*}{k} \right)$ has several Goldstone components which are linked.

2. Linked Cluster Theorem

The expression of the nth order perturbation energy implies a $(n-1)$-uple general summation which is written with a product of matrix elements between configurations Φ_K:

$$\sum_{I,J,K,...,M} \frac{\langle\Phi_0|V|\Phi_I\rangle\langle\Phi_I|V|\Phi_J\rangle\langle\Phi_J|V|\Phi_K\rangle\cdots\langle\Phi_M|V|\Phi_0\rangle}{(E_0-E_I)(E_0-E_J)(E_0-E_K)\dots(E_0-E_M)}$$

and some peculiar terms which involve the lower order corrections to the energy (ε^p) and the wave function (Ψ^q). For instance for the 3rd and 4th orders, if we use the intermediate normalization $(\langle 0|\Psi_q\rangle = 0, \forall q)$

$$\varepsilon^3 = \sum_{I,J\neq 0} \frac{\langle 0|V|\Phi_I\rangle\langle\Phi_I|V|\Phi_J\rangle\langle\Phi_J|V|0\rangle}{(E_0-E_I)(E_0-E_J)} - \varepsilon^1\langle\Psi^1|\Psi^1\rangle, \tag{1}$$
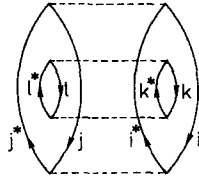
$$\varepsilon^4 = \sum_{I,J,K\neq 0} \frac{\langle 0|V|\Phi_I\rangle\langle\Phi_I|V|\Phi_J\rangle\langle\Phi_J|V|\Phi_K\rangle\langle\Phi_K|V|\Phi_0\rangle}{(E_0-E_I)(E_0-E_J)(E_0-E_K)} \tag{2}$$
$$- \varepsilon^1[\langle\Psi^1|\Psi^2\rangle + \langle\Psi^2|\Psi^1\rangle] - \varepsilon^2\langle\Psi^1|\Psi^1\rangle$$

The linked cluster theorem expresses cancellations between the general summation and the peculiar terms.

In our problem we make $\langle I|V|I\rangle = 0$. Then the linked cluster theorem only plays a role at the fourth order through $\varepsilon^2\langle\Psi^1|\Psi^1\rangle$. It is worthwhile to translate in molecular physics terms the illustration given by Brueckner [38] for the case of an electron gas.

The state Φ_i in Eq. (2) is characterized by a diexcitation process $\left(\dfrac{i^*j^*}{ij}\right)$. Now let us consider the state Φ_J obtained from a supplementary diexcitation: thus we obtain the quadriexcited state $\left(\dfrac{i^*j^*k^*l^*}{ijkl}\right)$. It is possible to go down to the ground state by many ways. We shall focuse our attention on two particular ways.

The first one consists in coming back through the same state $\Phi_i(\Phi_k = \Phi_i)$.

This leads to the preceeding unliked diagram and corresponds to the summation:

$$A = \sum_i\sum_j\sum_k\sum_l \frac{(ij|i^*j^*)(kl|k^*l^*)(k^*l^*|kl)(i^*j^*|ij)}{\left[\Delta E\left(\dfrac{i^*j^*}{ij}\right)\right]^2 \Delta E\left(\dfrac{i^*j^*k^*l^*}{ijkl}\right)}. \tag{3}$$

The second one consists in coming back through the state $\left(\dfrac{k^* \, l^*}{k \, l}\right)$ and is represented by the diagram of Fig. 2b. It gives the summation

$$B = \sum_i \sum_j \sum_k \sum_l \frac{(ij \mid i^* j^*)\,(kl \mid k^* l^*)\,(i^* j^* \mid ij)\,(k^* l^* \mid kl)}{\Delta E\!\left(\dfrac{i^* j^*}{ij}\right) \Delta E\!\left(\dfrac{i^* j^* k^* l^*}{ijkl}\right) \Delta E\!\left(\dfrac{k^* l^*}{kl}\right)}. \tag{4}$$

Let us consider now for given i, i^*, j, j^*, k, k^*, l and l^* the term in $\varepsilon^2 \langle \Psi^1 \mid \Psi^1 \rangle$ which comes from the contribution of $\left(\dfrac{i^* j^*}{ij}\right)$ in $\langle \Psi^1 \mid \Psi^1 \rangle$ and of $\left(\dfrac{k^* l^*}{kl}\right)$ in ε^2: we thus obtain

$$C = \frac{(ij \mid i^* j^*)^2 \,(kl \mid k^* l^*)^2}{\left[\Delta E\!\left(\dfrac{i^* j^*}{ij}\right)\right]^2 \Delta E\!\left(\dfrac{k^* l^*}{k \; l}\right)}. \tag{5}$$

Now one may notice that if $\Delta E\!\left(\dfrac{i^* j^* k^* l^*}{ijkl}\right) = \Delta E\!\left(\dfrac{i^* j^*}{ij}\right) + \Delta E\!\left(\dfrac{k^* l^*}{kl}\right)$ (additivity of transition energies), then

$$A + B - C = 0.$$

The unlinked diagrams contributions cancel with the particular terms. But there remain some terms in $\varepsilon^2 \langle \Psi^1 \mid \Psi^1 \rangle$ which have no corresponding elements in the general summation: these are the terms which involve at least one spin-orbital common in ε^2 and $\langle \Psi^1 \mid \Psi^1 \rangle$: for instance we cannot define a quadriexcited state from the two excitations $\left(\dfrac{i^* j^*}{ij}\right)$ and $\left(\dfrac{i^* k^*}{ik}\right)$, since it would violate the Pauli principle. For the purpose of simplification of the formulation of the linked cluster theorem, one sometimes introduces the remaining terms of the peculiar products in the general summation, where they give linked Exclusion Principle Violating (EPV; see Kelly 10) diagrams. The theorem is then expressed
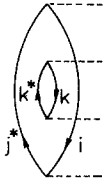
$$\varepsilon^n = \left(\left\langle 0 \left| V \left(\frac{Q_0}{a} V\right)^n \right| 0 \right\rangle\right) \quad \text{over all linked diagrams}$$

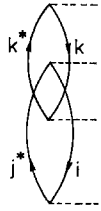where $\dfrac{Q_0}{a}$ is the reduced resolvent operator [42].

But such a trick would not be useful for our problem and would lead to a double number of remaining terms. We shall proceed in a more natural way and collect all the terms from $-\varepsilon^2 \langle \Psi^1 \mid \Psi^1 \rangle$ which would not be cancelled: we get the contribution of the EPV diagrams as the contributions of the states in $\varepsilon^2 \langle \Psi^1 \mid \Psi^1 \rangle$ which imply the same spin orbital in ε^2 and $\langle \Psi^1 \mid \Psi^1 \rangle$.

We shall make use of these cancellations between the general sum and the peculiar one only for the RS diagrams which reduce to a single Goldstone diagram. It is worthwhile to note that the cancellation occurs inside sets of RS diagrams from the general sum and one term from the peculiar sum. This property still holds when the RS diagram has several Goldstone components. Actually, the question of the

cancellation remains to be examined for those RS diagrams which are unlinked; as we have seen previously, they have linked and unlinked Goldstone components. Let us consider, for example, the three contributions
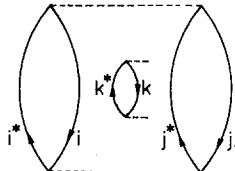

$$\left[\frac{\left\langle 0|V|\left(\dfrac{k^*}{k}\right)\right\rangle^2}{E_0 - E\left(\dfrac{k^*}{k}\right)}\right] \times \left[\frac{\left\langle 0|V|\left(\dfrac{j^*}{i}\right)\right\rangle}{E_0 - E\left(\dfrac{j^*}{i}\right)}\right]^2 .$$

$$\underbrace{\qquad\qquad}_{\text{from } \varepsilon^{(2)}} \qquad \underbrace{\qquad\qquad}_{\text{from } \langle \Psi^{(1)} | \Psi^{(1)} \rangle}$$

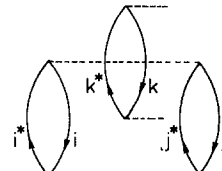(c_1) (c_2) (c_3)

The unlinked Goldstone components of the two diagrams would cancel with most of the terms arising from the peculiar contributions (c_3) when the numerator is expanded using mono and bielectronic integrals, and the total contribution of (c_1), (c_2) and (c_3) would be the sum of the linked terms of (c_1) and (c_2), and of the non cancelled terms of (c_3). But we may also remark that, owing to our assumptions of a correct polarity, the contributions of (c_2) and (c_3) are zero, since they both involve $\left\langle 0|V|\left(\dfrac{k^*}{k}\right)\right\rangle = 0$. The total contribution of (c_1), (c_2) and (c_3) is therefore simply equal to that of (c_1), namely

$$\frac{\left\langle 0|V|\left(\dfrac{j^*}{i}\right)\right\rangle^2 \left\langle \left(\dfrac{j^*}{i}\right)|V|\left(\dfrac{j^* k^*}{i k}\right)\right\rangle^2}{\left(E_0 - E\left(\dfrac{j^*}{i}\right)\right)^2 \left(E_0 - E\left(\dfrac{j^* k^*}{i k}\right)\right)} .$$

Therefore, concerning the unlinked RS diagrams with linked Goldstone components, we shall proceed by a direct calculation of the whole non zero RS diagrams (note that the three contributions may be zero, as in the following example):

$$\left[\frac{\left\langle 0|V|\left(\dfrac{k^*}{k}\right)\right\rangle^2}{E_0 - E\left(\dfrac{k^*}{k}\right)}\right] \times \left[\frac{\left\langle 0|V|\left(\dfrac{i^* j^*}{ij}\right)\right\rangle}{E_0 - E\left(\dfrac{i^* j^*}{ij}\right)}\right]^2$$

$$\underbrace{\qquad\qquad}_{\text{from } \varepsilon^{(2)}} \qquad \underbrace{\qquad\qquad}_{\text{from } \langle \Psi^{(1)} | \Psi^{(1)} \rangle}$$

The 2nd and 3rd contributions are zero since they involve $\left\langle 0|V|\left(\dfrac{k^*}{k}\right)\right\rangle$ and the 1st one involves $\left\langle\left(\dfrac{i^*j^*}{ij}\right)|V|\left(\dfrac{i^*j^*k^*}{ijk}\right)\right\rangle = \left\langle 0\,|V|\left(\dfrac{k^*}{k}\right)\right\rangle - [(ik\,|\,ik^*) + (jk\,|\,jk^*)]$
$+ [(i^*k\,|\,i^*k^*) + (j^*k\,|\,j^*k^*)] = 0,$ since $(ik\,|\,ik^*) = (i^*k\,|\,i^*k^*)$ and $(jk\,|\,jk^*)$
$= (j^*k\,|\,j^*k^*)$ taking into account the ZDO assumptions if i and j are not polar.

3. Perturbation Expansion Used

In classical correlation problems several partitions of the exact Hamiltonian have been proposed. From Møller and Plesset [43], one generally uses the partition

$$H_{exact} = H_{SCF} + V$$

and take the Hartree-Fock Hamiltonian as unperturbed Hamiltonian. The energy differences in the denominators are then differences between monoelectronic energies. This implies that there are large diagonal matrix elements in the perturbation matrix and makes the perturbation convergence slower [22]. It is worthwhile to use another partition, first proposed by Epstein [44] and by Nesbet [45]

$$H_0' = H_{SCF} + \sum_I \langle\Phi_I|V|\Phi_I\rangle\,|\Phi_I\rangle\,\langle\Phi_I|$$

$$V' = V - \sum_I \langle\Phi_I|V|\Phi_I\rangle\,|\Phi_I\rangle\,\langle\Phi_I|$$

where the Φ_I are the configurations of the basis. In that case, the energy differences in the denominators are differences between mean values of the exact Hamiltonian $\langle\Phi_I|H_0'|\Phi_I\rangle = \langle\Phi_I|H|\Phi_I\rangle$ and $\langle\Phi_I|V'|\Phi_I\rangle = 0$. The main defect of this method is that the "transition energies" are no longer additive: the "excitation energy" due to the diexcited configuration $\left(\dfrac{j^*\,\overline{l}^*}{ik}\right)$ is no longer the sum of the excitations energies of the two configurations $\left(\dfrac{j^*}{i}\right)\left(\dfrac{l^*}{k}\right)$. However, we have seen that this property was a necessary condition for the validity of the un-linked cluster cancellation.

In our case we can of course define an approximate Hamiltonian as a sum of monoelectronic Hamiltonians, of which the FLBO would be eigenfunctions, with eigenvalues equal to e_i or e_i^*.

$$e_i = \langle i\,|h|\,i\rangle + \sum_j^{occ.} (2J_{ij} - K_{ij}).$$

This zeroth-order Hamiltonian would be of the Møller-Plesset type (see Steiner [46]).

But it seems less artificial to define the zeroth order Hamiltonian by its diagonal elements

$$\langle\Phi_I|H_0''|\Phi_I\rangle = \langle\Phi_I|H|\Phi_I\rangle \forall\,I$$

and its non-diagonal elements:

$$\langle \Phi_I | H_0'' | \Phi_J \rangle = 0 \,, \; \forall \; I \neq J \,.$$

This partition is an Epstein-Nesbet type partition, and does not require an explicitation of the zeroth-order and perturbation Hamiltonians.

In fact we only want to go to fourth order of the perturbation expansion, and we do not take care of the definition of the zeroth-order energies of the configurations which are not implied at this order. We want to combine the advantages of the Epstein-Nesbet partition and of the linked cluster theorem. This theorem only begins to work at the fourth order in our problem. Thus we define the energies of the configurations implied in the first order correction [3] to the wave function as the mean values of the exact Hamiltonian. This insures the nullity of all elements $\langle \Phi_i | V'' | \Phi_i \rangle$ which could appear in third and fourth order terms. But we shall define the energies of the other diexcited configurations and of the tri and quadriexcited states in such a way that the linked cluster conditions are satisfied. It will be seen in Paper II that it is always possible. For instance we shall use

$$E\left(\frac{j^* \, \bar{l}^*}{i \, \bar{k}} \right) - E_0 = - E_{ij^*} - E_{kl^*}$$

instead of $\Delta E\left(\dfrac{j^* \, i^*}{l \; k} \right)$ which is the difference between the two mean values. This procedure introduces small diagonal terms in the perturbation matrix which would play a role at 5th and higher orders.

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[3] I.e. the mono and diexcited ones.

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