Revisión *Revista Mexicana de Física* **38**, *No. 2 (1992) 179–204*

Diagrammatic second order Möller-Plesset multi-reference perturbation theory

ALEJANDRO RAMÍREZ SOLÍS
SGIA, IBP, Instituto Mexicano del Petróleo
Eje Central Lázaro Cárdenas 152,
Apartado postal 14-805, 07730 México, D.F., México

Recibido el 15 de abril de 1991; aceptado el 2 de septiembre de 1991

ABSTRACT. A general scope of the many body perturbation theory (MBPT) is given to deal with electronic correlation effects in molecular systems. The fundamentals of the diagrammatic techniques are presented and we apply them to formulate the second order Möller-Plesset multireference perturbation theory (MR-MP2). The differences and similarities of the Epstein-Nesbet and Möller-Plesset partitions of the electronic hamiltonian are discussed. A comparison of the efficiency of standard MP2 and the diagrammatic approach is made for many molecular systems with different number of electrons and determinants in the reference space. The diagrammatic approach is 6 to 40 times faster than the standard programming depending on the features of the reference space.

RESUMEN. Se hace una revisión sucinta y general de la teoría de perturbación de muchos cuerpos (MBPT) aplicada al tratamiento de los efectos de correlación electrónica en sistemas moleculares. Se presentan los fundamentos de las técnicas diagramáticas y se aplican para formular la teoría multireferencial de perturbación de segundo orden Möller-Plesset (MR-MP2). Se discuten las diferencias, ventajas y similitudes entre las particiones Möller-Plesset y Epstein-Nesbet del hamiltoniano electrónico. Se compara la eficiencia de la versión diagramática con el algoritmo MR-MP2 stándard para varios sistemas moleculares con diferentes números de electrones, de orbitales moleculares y de determinantes en el espacio de referencia. El programa diagramático es entre 6 y 40 veces más rápido que el programa stándard, dependiendo del tamaño y tipo de excitaciones en el espacio de referencia.

PACS: 71.10.+x

1. INTRODUCTION

1960 can be called the year that the quantum mechanical study of molecular structure, spectra and reactivity began. Mulliken asked that very same year "what are electrons really doing in molecules?". The answer to Mulliken's question lies in the solution of the electronic Schrödinger equation

$$\hat{H}\Psi_i = E_i\Psi_i, \tag{1}$$

where we have used the well known Born-Oppenheimer approximation. This ansatz states that since nuclei are a lot heavier than electrons, it is possible to decouple their movements, the latter adjusting quasi-statically to the change in position of the former.

In Eq. (1), Ψ_i represents the wave function whose density $|\Psi_i|^2$ provides a description of the whole electronic ensemble in the molecule. For different integers i, different electronic states are obtained, $i = 0$ being the ground state. Electronic spectra (visible and UV) come from differences among E_i. When E_0 (the ground state energy) is lower than for separated atoms or smaller fragments, a bond is formed and chemists say that the complex is more stable than its separate constituents.

The Hamiltonian operator in Eq. (1) is made up of the kinetic contributions of all the electrons, of the electron-nucleus attractions and of the nucleus-nucleus and electron-electron repulsions. Since we want to solve Eq. (1) using the position of the nuclei as parameters (Born-Oppenheimer approximation) the electron-electron term in the Hamiltonian is called a two-particle operator: $1/r_{12}$ depending on the coordinates of two electrons. Because of this term, exact solutions of the Schrödinger equation are not possible even for H_2. Quantum chemistry is the science of developing the best possible *approximate* solutions to Eq. (1).

As we mentioned before, the electronic Schrödinger equation is normally solved for a given set of positions for the nuclei in the molecule: $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \ldots, \mathbf{R}_N)$. As the nuclei are moved, $E_i(\mathbf{R})$ spans a multi-dimensional energy surface for each electronic state i. $E_i(\mathbf{R})$ constitutes the potential energy for the vibrational and rotational Schrödinger equations that describe the quantized motions of the nuclei. Hence the solution to the electronic Schrödinger equation as a function of $\mathbf{R}$ provides nearly everything one wants to know about molecules. Nowadays, it is frequent to calculate not only $E_i(\mathbf{R})$ but also its gradient. When the gradient vanishes, a critical point is obtained and, depending upon the second derivative, it may be a minimum energy configuration which provides the actual molecular geometry or a "saddle point" in which case we are dealing with a transition state.

Although much profitable research can be done with semi-empirical approaches where the electronic Hamiltonian is simplified, we shall deal here only with first principle or *ab initio* methods.

There is now a wide variety of *ab initio* methods. They range in complexity from the well known Hartree-Fock Self-Consistent-Field (HF-SCF) to Multi-configurational SCF (MCSCF), Configuration Interaction (CI) in its various modalities like Singles and Doubles CI (SDCI), Multireference Configuration Interaction (MRCI), Coupled Cluster (CC) in its various approximations (LCCD, CCD, CCSD, CCSD-T1, CCSDT, CCSDTQ), Quadratic Configuration Interaction (QCI) and what is commonly called "many body perturbation theory" (MBPT). This paper is concerned with the last type of methods.

In the following section we will recall the basics of our starting point, the Hartree-Fock theory and we shall answer why the electronic correlation effects are of utmost importance if we want to achieve the final goal of quantum chemistry: to be predictive, *i.e.*, to yield quantitative results in the absence of experimental ones, or to give a third opinion when experimental discrepancies exists. To that end, it is most often necessary to obtain *ab initio* solutions for the Schrödinger equation that go much further than the simplest of these methods (HF-SCF), which does not take into account these correlation effects.

In Section 3 we introduce the basic principles of the many body perturbation theory. We also show the differences and similarities between the Möller-Plesset (MP) and the Epstein-Nesbet (EN) partitions of the electronic Hamiltonian.

In Section 4 the fundamentals of the diagrammatic technique to deal with electronic correlation for a single reference wave function are given. We shall present the advantages of using these techniques and explicitly develop the diagrammatic approach to the second order Möller-Plesset perturbation theory.

In Section 5 we present the diagrammatic approach for the second order energy contribution of a reference wave function containing more than a single determinant. All the possible cases are given and explicit diagrams as well as their corresponding algebraic formulas are presented.

Finally, in Section 6, a comparison of the relative efficiency of the diagrammatic to the standard CIPSI algorithms is made for many molecular systems of varying size and different number of determinants in the reference space.

2. THE HARTREE-FOCK MODEL AND ELECTRONIC CORRELATION

Before we develop the perturbation theory we must say that our starting point will be the Hartree-Fock theory in its restricted version (RHF). In this approach, the ground state wave function $|\Phi_0\rangle$ is constructed as a Slater determinant by occupying twice the lowest-lying $\phi_1, \phi_2, \ldots, \phi_{n/2}$ molecular orbitals (MO)

$$|\Phi_0\rangle = |\phi_1(1)\bar{\phi}_1(2)\cdots\phi_{n/2}(n-1)\bar{\phi}_{n/2}(n)|.$$

It is well known that from the properties of a determinant we get the Pauli Exclusion Principle and that the anti-symmetric property for fermion systems is automatically satisfied.

The orbitals ϕ_i are constructed supposing that an electron in a given orbital only "feels" the average potential generated by the remaining $n-1$ electrons. This means that we are using a single-particle model where a set of integro-differential equations,

$$\hat{f}(1)\phi_i(1) = \varepsilon_i\phi_i(1) \qquad (i = 1, 2, \ldots, N), \tag{2}$$

replaces the real multi-particle problem of Eq. (1). Here N stands for the dimension of the atomic set used to span the basis in which the molecular orbitals ϕ_i are developed, ε_i represent the orbital energies and the Fock operator is given by

$$\hat{f}(1) = \hat{h}(1) + \hat{v}^{\mathrm{HF}}(1), \tag{3}$$

where

$$\hat{h}(1) = -\nabla^2/2 + \sum_{\alpha} \frac{Z_\alpha}{r_{1\alpha}}$$

and α runs over all the nuclei.

The average (Hartree-Fock) potential that a given electron sees is

$$\hat{v}^{\mathrm{HF}}(1) = \sum_{a}^{\mathrm{occ}} 2\hat{J}_a(1) - \hat{K}_a(1), \tag{4}$$

the a index extending over all the occupied orbitals.

$\hat{J}$ and $\hat{K}$ are the Coulomb and exchange operators defined by

$$\hat{J}_a(1)\phi_b(1) = \left[\int \phi_a(2)\frac{1}{r_{12}}\phi_a(2)\,d\tau_2\right]\phi_b(1)$$

and

$$\hat{K}_a(1)\phi_b(1) = \left[\int \phi_a(2)\frac{1}{r_{12}}\phi_b(2)\,d\tau_2\right]\phi_a(1).$$

Note that $\hat{K}$ is a non-local operator since it depends on the value of ϕ_b over all space.

Here we should mention that although the HF model does not allow two electrons having the same spin to be in the same spatial region (Fermi hole) and thus accounts for some of the electronic correlation, it is said that the HF approach is a non-correlated model because it does not take into account the instantaneous repulsion introduced by the $1/r_{12}$ term in the Hamiltonian. With this independent-particle model we have neglected the singularity that arises when $\mathbf{r}_1$ tends to $\mathbf{r}_2$ and we have thus ignored the Coulomb hole that surrounds each electron.

The correlation energy of a given state I is defined as the difference between the exact non-relativistic energy of that state and the Hartree-Fock energy [1]

$$E_I^{\text{corr}} = E_I - E_I^{\text{HF}},$$

with

$$E_I = \frac{\langle\Psi_I|H|\Psi_I\rangle}{\langle\Psi_I|\Psi_I\rangle}$$

and

$$E_I^{\text{HF}} = \frac{\langle\Phi_I|H|\Phi_I\rangle}{\langle\Phi_I|\Phi_I\rangle},$$

where $|\Phi_I\rangle$ is the Hartree-Fock determinant that describes the state under consideration and $|\Psi_I\rangle$ represents the exact solution of Eq. (1).

The electronic correlation effects are those not accounted for by the HF model, namely, those that arise due to the instantaneous interaction between each couple of electrons. In other words, electronic correlation is the difference between the exact n-body solution $|\Psi_I\rangle$ (projected onto the finite-dimensional Hilbert space we have chosen) and the solution of the Hartree-Fock independent-particle model.

Quantum chemists distinguish between two essential types of electronic correlation. Non-dynamic correlation appears when we consider a wave function that includes excitations to valence virtual orbitals while dynamic correlation appears only when we include determinants involving excitations to higher-lying non-valence virtual orbitals. These non-valence virtual orbitals arise when we include atomic orbitals in the basis set of higher ($l = l_{\mathrm{val}} + 1, 2, \ldots$) angular momentum than the highest occupied atomic orbital corresponding to l_{val}.

The following theory can also be used when we are dealing with an odd number of electrons and when considering one or many open shells. This is called Restricted open Shell HF theory (ROSHF) [2].

3. MANY BODY PERTURBATION THEORY

This section deals with the perturbation expansion of the Rayleigh-Schrödinger type for the total energy and wave function. In the linked-diagram formulation this is commonly called many body perturbation theory (MBPT). Closely related to MBPT are the coupled cluster (CC) methods, which are equivalent to the infinite summation of certain classes of terms appearing in the MBPT expansion.

Historically, the perturbative approach to treat electronic correlation dates back to 1934 when Möller and Plesset [3] first applied it to many electron systems. One of the reasons why quantum chemists are using perturbative techniques is because these methods are (in the Möller-Plesset version) "size-extensive", *i.e.*, the electronic correlation energy they yield scales linearly with the number of particles, unlike many variational (configuration interaction) schemes.

We shall start with the unperturbed Schrödinger equation:

$$\hat{H}_0|\Phi_I\rangle = E_I^0|\Phi_I\rangle \qquad (I = 0, 1, 2, \ldots), \tag{5}$$

where $|\Phi_I\rangle$ are all the possible determinants that can be constructed using a given set of N molecular orbitals and n electrons. The working hypothesis is that both, the energy and the wave function for any state I can be expanded in a power series of a parameter λ that defines the intensity of the perturbation V

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \qquad (\lambda \in R\ [0, 1])$$

$$E_I = E_I^0 + \lambda E_I^{(1)} + \lambda^2 E_I^{(2)} + \lambda^3 E_I^{(3)} + \cdots, \tag{6}$$

$$|\Psi_I\rangle = |\Phi_I\rangle + \lambda|\Psi_I^{(1)}\rangle + \lambda^2|\Psi_I^{(2)}\rangle + \lambda^3|\Psi_I^{(3)}\rangle + \cdots. \tag{7}$$

The physical problem we want to solve is given by $\lambda = 1$:

$$(\hat{H}_0 + \lambda\hat{V})|\Psi_I\rangle = E_I|\Psi_I\rangle \qquad (I = 0, 1, 2, \ldots). \tag{8}$$

We suppose that the space spanned by all the zeroth-order states $|\Phi_I\rangle$ is complete and develop the i-th order wave functions as

$$|\Psi_I^{(i)}\rangle = \sum_{J \neq I} C_J^{(i)}|\Phi_J^{(i)}\rangle. \tag{9}$$

If we introduce the expressions given by Eqs. (6) and (7) into Eq. (8) it is possible to identify on each side of the resulting equation the coefficients of a given power of λ. It is interesting to see explicitly what the lowest orders yield.

At the zeroth order we get the equivalent of Eq. (5),

$$\hat{H}_0|\Phi_0\rangle = E_0^0|\Phi_0\rangle, \tag{10}$$

if we are interested in the ground state, which is normally the case. The excited states can be formally treated in exactly the same manner but in practice we are sometimes confronted with convergence problems or quasi-degeneracies that lead to uneasy situations.

At the first order we have

$$\hat{H}_0|\Psi_I^{(1)}\rangle + \hat{V}|\Phi_I\rangle = E_I^0|\Psi_I^{(1)}\rangle + E_I^{(1)}|\Phi_I\rangle. \tag{11}$$

Multiplying (11) by $\langle\Phi_I|$ we get

$$E_I^0\langle\Phi_I|\Psi_I^{(1)}\rangle + \langle\Phi_I|\hat{V}|\Phi_I\rangle = E_I^0\langle\Phi_I|\Psi_I^{(1)}\rangle + E_I^{(1)}\langle\Phi_I|\Phi_I\rangle,$$

but the first order correction $|\Psi_I^{(1)}\rangle$ is orthogonal to $|\Phi_I\rangle$. This leads us to

$$E_I^{(1)} = \langle\Phi_I|\hat{V}|\Phi_I\rangle, \tag{12}$$

which states that the first order energy is nothing more than the expectation value of the perturbation for the zeroth order wave function.

In order to get the expansion coefficients $C_I^{(1)}$, we multiply Eq. (11) by $\langle\Phi_J|$

$$\langle\Phi_J|\hat{H}_0|\Psi_I^{(1)}\rangle + \langle\Phi_J|\hat{V}|\Phi_I\rangle = E_I^0\langle\Phi_J|\Psi_I^{(1)}\rangle + E_I^{(1)}\langle\Phi_J|\Phi_I\rangle,$$

$$E_J^0\langle\Phi_J|\Psi_I^{(1)}\rangle + \langle\Phi_J|\hat{V}|\Phi_I\rangle = E_I^0 C_J^{(1)},$$

therefore

$$C_J^{(1)} = \frac{\langle\Phi_J|\hat{V}|\Phi_I\rangle}{E_I^0 - E_J^0}. \tag{13}$$

This allows us now to write the total wave function up to first order as

$$|\Psi_I\rangle^1 = |\Phi_I\rangle + |\Psi_I^{(1)}\rangle = |\Phi_I\rangle + \sum_{J\neq I} \frac{\langle\Phi_J|\hat{V}|\Phi_I\rangle}{E_I^0 - E_J^0}|\Phi_J\rangle. \tag{14}$$

In the case where the ground state is the closed shell HF determinant, Brillouin's theorem restricts $|\Phi_J\rangle$ to the di-excited determinants one can construct from $|\Phi_0\rangle$; the overall first order wave function takes the form

$$|\Psi_0\rangle^1 = |\Phi_0\rangle + |\Psi_0^{(1)}\rangle = |\Phi_0\rangle + \sum_{J \text{ diex}} \frac{\langle\Phi_J|\hat{V}|\Phi_0\rangle}{E_0^0 - E_J^0}|\Phi_J\rangle;$$

while the second order correction to the energy is given by

$$E_0^{(2)} = \sum_{J \text{ diex}} \frac{\langle \Phi_0 | \hat{V} | \Phi_J \rangle \langle \Phi_J | \hat{V} | \Phi_0 \rangle}{E_0^0 - E_J^0}. \tag{15}$$

As a general rule, the even and odd order energies can be written as [4,5]

$$E_I^{(2K)} = \langle \Psi_I^{(K)} | \hat{V} | \Psi_I^{(K-1)} \rangle - \sum_{M=1}^{K} \sum_{N=1}^{K-1} E_I^{(2K-M-N)} \langle \Psi_I^{(M)} | \Psi_I^{(N)} \rangle \tag{16}$$

and

$$E_I^{(2K-1)} = \langle \Psi_I^{(K-1)} | \hat{V} | \Psi_I^{(K-1)} \rangle - \sum_{M=1}^{K-1} \sum_{N=1}^{K-1} E_I^{(2K-1-M-N)} \langle \Psi_I^{(M)} | \Psi_I^{(N)} \rangle. \tag{17}$$

The last double sums are called the "normalization terms" (NT) because of the scalar product between the M-th and N-th order corrections to the wave function. Equations (16) and (17) can both be written in a more compact form as

$$E_I^{(K)} = \langle \Phi_I | \hat{V} | \Psi_I^{(K-1)} \rangle \tag{18}$$

and the wave function

$$|\Psi_I^{(K)} \rangle = \hat{R} \hat{V} | \Psi_I^{(K-1)} \rangle - \sum_{M=1}^{K-1} E_I^{(K)} \hat{R} | \Psi_I^{(K-M)} \rangle, \tag{19}$$

where

$$\hat{R} = \sum_{J \neq I} \frac{|\Phi_J \rangle \langle \Phi_J |}{E_I^0 - E_J^0}.$$

Introducing (19) into Eq. (18) leads us to

$$E_I^{(K)} = \langle \Phi_I | \hat{V} (\hat{R} \hat{V})^{(K-1)} | \Phi_I \rangle - \text{NT}. \tag{20}$$

The number of terms in the normalization part (NT) grows very rapidly and the simplest way to calculate them is using the technique developed by Brueckner [6]. It is this normalization part that is responsible for the incorrect size-extensive behavior if we omit it.

A. The Möller-Plesset partition of the Hamiltonian

In atomic physics $\hat{H}_0$ is sometimes used as the simple sum of mono-electronic Hamiltonians

$$\hat{H}_0 = \sum_i h_i = \sum_i -\tfrac{1}{2}\nabla_i^2 + \frac{Z}{r_i};$$

nevertheless, in molecular physics $\hat{H}_0$ is usually written as the Hartree-Fock Hamiltonian

$$\hat{H}_0 = \sum_i \hat{f}(i) = \sum_i \hat{h}(i) + \hat{v}^{\mathrm{HF}}(i). \tag{21}$$

The Möller-Plesset partition of the overall hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$ uses $\hat{H}_0$ as defined in Eq. (21). The perturbation is then the difference of the two-electron operator and the average HF potential

$$\hat{V} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i \hat{v}^{\mathrm{HF}}(i).$$

The advantage of this choice is that the corrections to the energy and the wave functions arise directly from the correlation effects, strictly speaking.

Another common choice is the Epstein-Nesbet (EN) partition of the electronic Hamiltonian [7] in which $\hat{H}_0$ is taken as the diagonal terms of the Hamiltonian matrix constructed using all the determinants built from the canonical (HF) molecular orbitals. $\hat{V}$ is only composed of the non-diagonal terms since we have included $\langle\Phi_I|\hat{V}|\Phi_I\rangle$ in $\hat{H}_0$. We must point out that the EN version of the MBPT is not size-extensive. This is one of the reasons why most quantum chemistry programs perform 2nd, 3rd or even 4th order Möller-Plesset (MP2, MP3, MP4) calculations.

Claverie *et al.* [7] showed that the EN partition leads to a faster convergence of the perturbation series than the MP one. However, for a low perturbation order, the former can lead to absurd results for transition energies, in particular if one the states under consideration is represented, at the zeroth order, by a linear combination of non-degenerate determinants [20].

Since in the MP approach the zeroth order energies E_I^0 are simply the sum of the energies of the occupied spin-orbitals in state $|\Phi_I\rangle$,

$$E_I^0(\mathrm{MP}) = \sum_k^{\mathrm{occ}} \varepsilon_k \qquad (k \text{ occupied in } |\Phi_I\rangle), \tag{22}$$

to obtain the corresponding energies in the EN partition, we have to add to these the diagonal terms of $\hat{V}$:

$$E_I^0(\mathrm{EN}) = E_I^0(\mathrm{MP}) + \langle\Phi_I|\hat{V}|\Phi_I\rangle. \tag{23}$$

The size-inextensivity of the Epstein-Nesbet version of MBPT comes from the definition of the energy differences in the denominators of the perturbation expansion. Since these denominators cannot be written anymore as simple differences of orbital energies, the EN partition does not satisfy the conditions of the Linked-Cluster theorem [8].

4. FUNDAMENTALS OF THE DIAGRAMMATIC APPROACH

Perturbation theory becomes more and more complicated as higher orders are considered. For this reason Feynman [9] developed the diagrammatic approach to apply it to quantum electrodynamics (QED). Some years later, Goldstone [10] adapted this technique to the MBPT and verified that Brueckner's hypothesis regarding the good behavior (linear scaling with the number of particles) of MBPT was true, order by order. Some other diagrammatic representations such as Hugenholtz's exist, but we shall present here the most widely used one, namely, the one developed by Goldstone.

Diagrams are graphic structures generated according to a few mnemotechnic rules that allow us to derive in a simple way the corresponding algebraic expressions. The problem of finding the expressions of Eqs. (18) and (19) in terms of molecular integrals is greatly simplified if one uses the diagrammatic technique. Many authors think that diagrams have more physical content than the complicated equations they represent and are also simpler to manipulate.

Diagrams are also a very helpful tool to analyze different aspects of electronic correlation. They can be used to create new perturbative techniques, defined in terms of certain classes of diagrams having a common feature rather than using the classical order by order criterion. In this way it has been possible to sum a certain class of diagrams to infinite order [11]

There are a certain number of applications and quantum chemistry packages that use these techniques [12-16].

At this point we need to introduce the following common notation for molecular integrals (after an N^5 transformation from the atomic basis set to the molecular one)

$$\langle ab|cd\rangle = \int\int \phi_a^*(1)\phi_b^*(2)\frac{1}{r_{12}}\phi_c(1)\phi_d(2)\,d\tau_1\,d\tau_2,$$

$$\langle ab||cd\rangle = \langle ab|cd\rangle - \langle ab|dc\rangle.$$

The matrix elements of the Fock operator in the molecular basis are

$$\hat{F}^0_{ab} = \langle a|\hat{F}|b\rangle = \langle a|\hat{h}|b\rangle + \sum_i^{\text{occ}} 2\langle a|\hat{J}_i|b\rangle - \langle a|\hat{K}_i|b\rangle, \tag{24}$$

where the 0 label tells us that the i-index runs over all the occupied orbitals in the HF $|\Phi_0\rangle$ reference.

From here onwards we will use a, b, c, d for occupied orbitals (holes) in $|\Phi_0\rangle$, r, s, t, u for virtual orbitals (particles) and i, j, k, l to denote arbitrary orbitals.

With that convention, a doubly excited determinant with respect to $|\Phi_0\rangle$ in which we take two electrons from orbitals a and b to put them into orbitals r and s is expressed in second quantized form as

$$|\Phi_{ab}^{rs}\rangle = \hat{a}_r^+ \hat{a}_s^+ \hat{a}_a \hat{a}_b |\Phi_0\rangle.$$

Recall that the creation and annihilation operators must be applied from right to left.

We can now write Eqs. (15.a) and (15.b) in terms of molecular integrals. If we take $|\Phi_0\rangle$ as the closed shell HF determinant of the ground state, the first order contribution to the wave function is

$$|\Psi_0^{(1)}\rangle = \sum_{a<b}\sum_{r<s} \frac{\langle \Phi_{ab}^{rs}|\hat{V}|\Phi_0\rangle}{E_0^0 - E_{ab}^{rs}} |\Phi_{ab}^{rs}\rangle,$$

which can be written in second quantized form as

$$|\Psi_0^{(1)}\rangle = \frac{1}{2}\sum_{a,b}\sum_{r,s} \frac{\langle ab\|rs\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} \hat{a}_r^+ \hat{a}_s^+ \hat{a}_a \hat{a}_b |\Phi_0\rangle. \qquad (25)$$

The second order energy $E_0^{(2)} = \langle \Phi_0|\hat{V}|\Psi_0^{(1)}\rangle$ is then

$$E_0^{(2)} = \sum_{a<b}\sum_{r<s} \frac{\langle \Phi_0|\hat{V}|\Phi_{ab}^{rs}\rangle\langle \Phi_{ab}^{rs}|\hat{V}|\Phi_0\rangle}{E_0^0 - E_{ab}^{rs}}.$$

We write this last equation in terms of molecular integrals using Slater's rules:

$$E_0^{(2)} = \frac{1}{2}\sum_{a,b}\sum_{r,s} \frac{\langle ab\|rs\rangle\langle rs\|ab\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}. \qquad (26)$$

We can now give the simple rules for the diagrammatic approach:

— The interaction between two electrons is represented by a broken line

$$\hat{V} \equiv \circ\!-\!-\!-\!-\!-\!-\!\circ$$

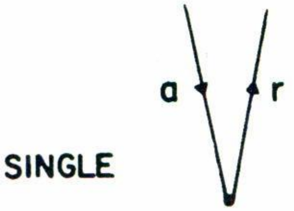
— The occupied (holes) and virtual (particles) orbitals are represented by downward and upward lines respectively

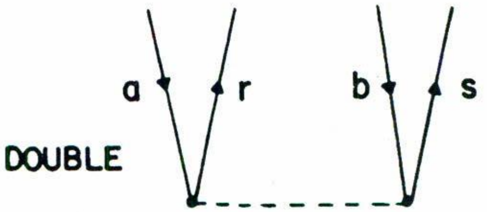
$$\downarrow a \qquad r \uparrow$$

— We will consider the HF closed shell determinant as our reference (vacuum) state. Diagrammatically this is

$$|\Phi_0\rangle \equiv$$

— Single and double excitations from the vacuum are then



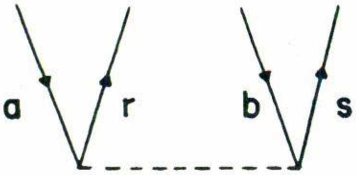


— To calculate the coefficients of the n-th order wave functions, the numerator is given by products of the corresponding mono-electronic F_{ab} or bi-electronic $\langle ab|rs\rangle$ interactions while the denominator is given by the orbital energies of the particles we are creating minus the orbital energies of the holes.

— A minus sign appears every time an interaction between two lines of the same type appears

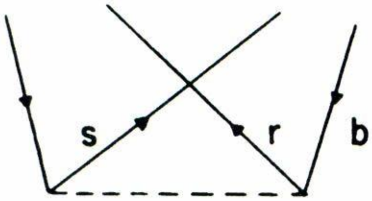
— A minus sign appears every time two lines of the same type intersect

Let us now draw the diagram corresponding to the first order correction to the wave function



$$\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab|rs\rangle}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b}$$

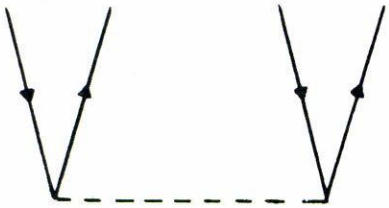
and



$$-\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab|sr\rangle}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b}.$$

The crossing of two lines of the same type (in this case two particles) is translated into a minus sign.

We represent generically both diagrams without labels



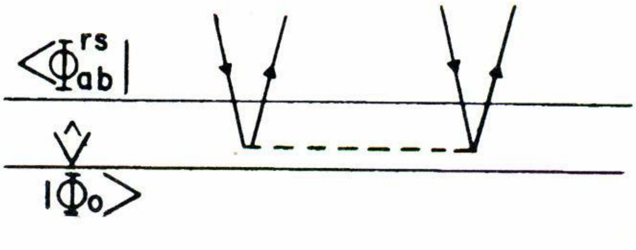
$$\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab||rs\rangle}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b} \tag{27}$$

and see that we get the same expression as in (25) for the first order coefficients of the wave function.

The existence of many particular orders of holes and particles reflects the fact that when two electrons are excited from orbitals a and b to r and s, we cannot distinguish between the following processes

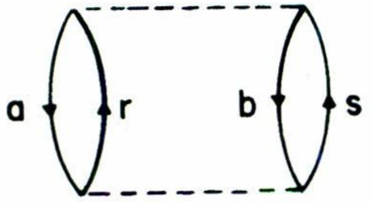
We have thus to introduce a 1/2 factor in front of each of these diagrams.

Note that since we decided to use $|\Phi_0\rangle$ as the vacuum state, the diagrams



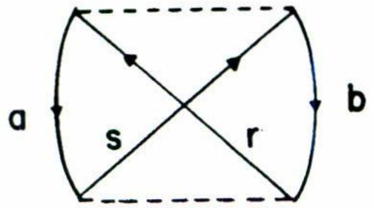
take us out the reference space because they are open ended in the upper part, the coefficient of each di-excitation being given by Eq. (27).

If we want to calculate the second order energy using the diagram (27) for $|\Psi_I^{(1)}\rangle$ and $E_0^{(2)} = \langle\Psi_0|\hat{V}|\Psi_I^{(1)}\rangle$, we have to close (27) with another broken line ($\hat{V}$) above to end again on the vacuum state $|\Psi_0\rangle$ (no holes, no particles)



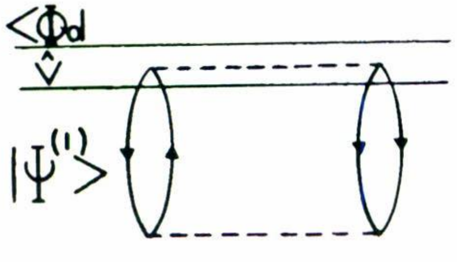
$$\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b} \tag{28a}$$

and



$$\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab|sr\rangle\langle rs|ab\rangle}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b}. \tag{28b}$$

The total of these two diagrams is



$$\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b} \tag{29}$$

which corresponds exactly to what we had found using Slater's rules in Eq. (26). The fact that there are two interaction lines in the diagram tells us that it corresponds to a second order energy. This is, of course, a general rule for any order k, where we would have k interaction lines.

An important point we should stress is that since we are dealing with the Möller-Plesset partition, the first order energy,

$$E_0^{(1)} = \langle\Phi_0|\hat{V}|\Phi_0\rangle = \langle\Phi_0|\frac{1}{r_{12}} - \hat{V}^{\mathrm{HF}}|\Phi_0\rangle$$

$$= \frac{1}{2}\sum_a^{\mathrm{occ}}\sum_b^{\mathrm{occ}}\langle ab||ab\rangle - \sum_a^{\mathrm{occ}}\langle a|\hat{v}^{\mathrm{HF}}|a\rangle$$

$$= \frac{1}{2}\sum_a^{\mathrm{occ}}\sum_b^{\mathrm{occ}}\langle ab||ab\rangle - \sum_a^{\mathrm{occ}}\sum_b^{\mathrm{occ}}\langle ab|ab\rangle - \langle ab|ba\rangle$$

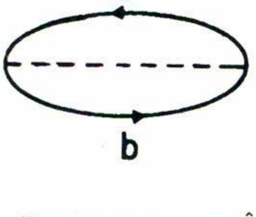
$$E_0^{(1)} = -\frac{1}{2}\sum_a^{\mathrm{occ}}\sum_b^{\mathrm{occ}}\langle ab||ab\rangle,$$

is already included in the Hartree-Fock energy

$$E_0^{\mathrm{HF}} = E_0^{(0)} + E_0^{(1)} = \sum_a^{\mathrm{occ}}\varepsilon_a - \frac{1}{2}\sum_a^{\mathrm{occ}}\sum_b\langle ab||ab\rangle.$$

Diagrammatically $-E_0^{(1)}$ is expressed as

$$\frac{1}{2}\sum_a^{\mathrm{occ}}\sum_b^{\mathrm{occ}}\langle ab|ab\rangle,$$

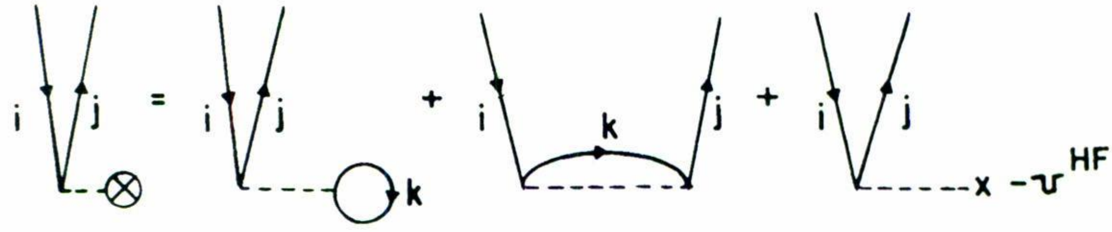


$$-\frac{1}{2}\sum_a^{\mathrm{occ}}\sum_b^{\mathrm{occ}}\langle ab|ba\rangle,$$

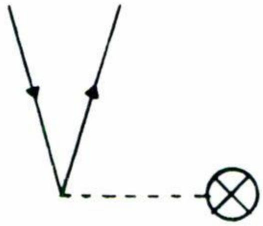
while the effective potential $\hat{V}$ is

$$V_{ij} = \langle i|\hat{V}|j\rangle = \left\langle i\left|\frac{1}{r_{12}} - \hat{V}^{\mathrm{HF}}\right|j\right\rangle$$

$$\langle i|\hat{V}|j\rangle = \sum_k(\langle ik|jk\rangle - \langle ik|kj\rangle) - \langle i|\hat{v}^{\mathrm{HF}}|j\rangle$$

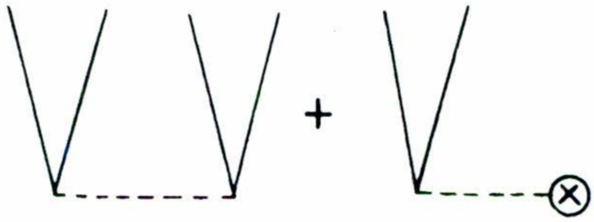


If we had not used the canonical HF molecular orbitals to construct the reference state, it would have been necessary to add diagrams of the type



to the first order correction of the wave function

$|\Psi_I^{(1)}\rangle \equiv$



but such is not the case thanks to Brillouin's theorem.

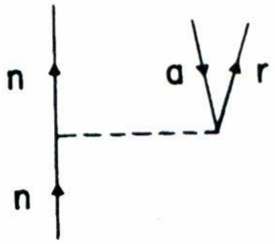
All this has been developed for a closed shell reference state but the diagrammatic approach can be extended to systems of one or more open shells. For instance, the state $|\Phi_0\rangle = |1, 2, \ldots, n-1, n\rangle$ can be obtained as $|\Phi_0\rangle = \hat{a}_n^+|0\rangle$ if the vacuum state is defined as $|0\rangle = |1, 2, \ldots, n-1\rangle$. In that case $|\Phi_0\rangle$ is not any longer the vacuum state but the diagram

$|\Phi_0\rangle \equiv$

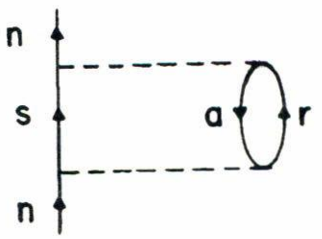
and the first order correction would be given by the single excitations interacting with

$|\Phi_0\rangle$, namely

$$|\Psi_0^{(1)}\rangle \equiv$$



while the second order energy would be



5. MULTI-REFERENCE SECOND ORDER MÖLLER-PLESSET PERTURBATION

Up to now we have considered only reference states containing a single determinant. Nevertheless, there are many cases where this approximation to the zeroth order wave function is not sufficient. The most common example of this is when a molecule is being torn apart and at least two determinants are necessary to properly describe the dissociation limit corresponding to neutral fragments $A + B$ (not the average of the ionic limits $A^- + B^+$ and $A^+ + B^-$). Another very common problem is found when one tries to use a single reference wave function near the crossing of potential energy surfaces where at least two configurations (one from the higher-lying state and one from the lower-lying one) interact strongly and must be included in the description of both electronic states.

There are a few applications of MBPT to multireference wave functions like those of Whitten and Hackenmayer [17], the MRD-CI of Buenker and Peyerimhoff [18,19] and the Configuration Interaction and Perturbation through Selected Iteration (CIPSI) approach of Malrieu *et al.* [20,21]. Only the last two algorithms have found wide acceptance among the quantum chemists. In the remaining of the paper we shall concentrate on the latter.

The basic idea underlying CIPSI is quite simple and can be explained in a few lines:

1) To perform a variational (configuration interaction) calculation to account for the largest interactions between the components (determinants) that provide a good zeroth order description of one or many states and

2) To account perturbatively for the small interactions between the zeroth-order wave function and all the determinants that are coupled with it up to second order.

Let us take $|\Psi_m^0\rangle$ as the zeroth order wave function for the m-th state

$$|\Psi_m^0\rangle = \sum_{I\in S} C_m^I |I\rangle, \tag{30}$$

where we have already chosen a set (S) of determinants $|I\rangle$ that span the reference space of dimension NCF here $|\Psi_m\rangle$ has its largest components.

If $\hat{P}_S = \sum_{I\in S} |I\rangle\langle I|$ is the projection operator onto the reference space, the diagonalization of H restricted to S,

$$\hat{P}_S \hat{H} \hat{P}_S |\Psi_m^0\rangle = E_m^0 |\Psi_m^0\rangle,$$

yields NCF zeroth order wave functions developed as in Eq. (30). The number of configurations in the reference space can be as large as 1000 (NCF $\leq$ 1000). This accomplishes the first step.

In order to account for the second order energy contribution, we must first stress that there are three possible choices for the zeroth order energies E_m^0: the first and the most natural one is to take directly the eigenvalue obtained for $\hat{P}_S \hat{H} \hat{P}_S$

$$E_m^0(\text{EEN}) = E_m^0,$$

where EEN stands for Eigenvalue Epstein-Nesbet. The second and third choices involve weighted means of the Möller-Plesset and Epstein-Nesbet energies of the determinants in S, for that reason they are called barycentric

$$E_m^0(\text{MPB}) = \sum_{I\in S} (C_m^I)^2 E_I^0(\text{MP}),$$

$$E_m^0(\text{ENB}) = \sum_{I\in S} (C_m^I)^2 E_I^0(\text{EN}),$$

where $E_I^0(\text{MP})$ and $E_I^0(\text{EN})$ correspond to Eqs. (22) and (23) while C_m^I are the variational expansion coefficients of state m in the reference space.

It has been shown [22] that for symmetric systems where the molecular orbitals are delocalized, if one uses any of the Epstein-Nesbet partitions (EEN or ENB), an artificial dependence on the reciprocal of the inter-atomic distance appears during the bond breaking process. On the other hand, a barycentric choice for E_m^0 is better suited to describe transition energies since a great deal of diagrams common to the perturbation expansions of both states annihilate [20].

The second order energy for a multireference wave function is

$$E_m^0 = \sum_{k\notin S} \frac{\langle \Psi_m^{(0)} | \hat{V} | K \rangle \langle K | \hat{V} | \Psi_m^{(0)} \rangle}{E_m^0 - E_K^0}, \tag{31}$$

where $|K\rangle$ represents determinants external to the reference space. Since we will develop the diagrammatic MP version of multireference MBPT,

$$E_K^0 = \sum_{i \in K} \varepsilon_i$$

is the energy of determinant $|K\rangle$, and E_m^0 is the MPB zeroth order energy of state m we have just defined.

If we substitute expression (30) in Eq. (31), we get

$$E_m^{(2)} = \sum_{K \notin S} \sum_{I,J} \sum_{\in S} \frac{\langle J|V|K\rangle\langle K|V|I\rangle C_m^I C_m^J}{E_m^0 - E_K^0}. \tag{32}$$

The idea of programming diagrammatically the CIPSI algorithm is originally due to Cimiraglia and Persico [23,24]. To that end they found it convenient to split Eq. (32) into

$$E_m^{(2)}(\text{diag}) = \sum_{K \notin S} \sum_{I \in S} (C_m^I)^2 \frac{\langle I|V|K\rangle\langle K|V|I\rangle}{E_m^0 - E_K^0} \tag{33}$$

and

$$E_m^{(2)}(\text{non-diag}) = \sum_{K \notin S} \sum_{I<J} \sum_{\in S} 2C_m^I C_m^J \frac{\langle J|V|K\rangle\langle K|V|I\rangle}{E_m^0 - E_K^0}. \tag{34}$$

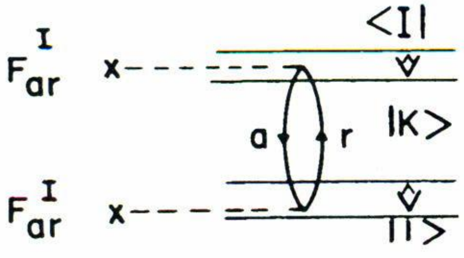
In the previous section we have seen how we could take a given determinant to be the vacuum state. When dealing with multireference wave functions it is very useful to consider each determinant belonging to S as a temporary vacuum.

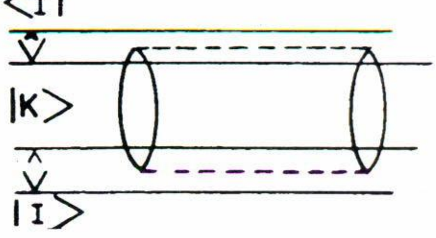
Let us first concentrate on the diagonal contribution. If we take $|I\rangle$ as a temporary vacuum, there are only two cases where $\langle K|V|I\rangle$ is non vanishing (recall that $|K\rangle$ must be out of the reference space):

1) If $|K\rangle$ is a singly-excited determinant with respect to $|I\rangle$ or

2) If $|K\rangle$ is a doubly-excited determinant with respect to $|I\rangle$.

Since we go from $|I\rangle$ to $|K\rangle$ and back to $|I\rangle$ we can draw the following diagrams





We must not forget that a shift was made to bring $|I\rangle$ to the vacuum temporarily, thus the associated Fock operator must accordingly be changed to

$$F^I_{ar} = F^0_{ar} + \left\langle a \left| \sum_p (\hat{J}_p - \hat{K}_p) - \sum_h (\hat{J}_h - \hat{K}_h) \right| r \right\rangle , \tag{35}$$

where F^0_{ar} is the Fock operator associated with the HF closed shell reference given in Eq. (24), and the p and h indexes mean that the sums must be extended over all the particles and holes of determinant $|I\rangle$.

The energetic contributions of diagrams 1) and 2) are

1) $$\sum_{I \in S} \sum_{a \in I} \sum_{r \in I} \frac{F^I_{ar} F^I_{ra}}{E^0_m - E^0_K}$$

2) $$\sum_{I \in S} \sum_{a,b \in I} \sum_{r,s \in I} \frac{|\langle ab||rs\rangle|^2}{E^0_m - E^0_K}$$

Clearly, the quintuple sum in the last expression is very computationally demanding, the time being proportional to NCF $\times N^2_{\text{occ}} \times N^2_{\text{virt}}$. To give an idea of a typical calculation, NCF $\cong 300$, $N_{\text{occ}} \cong 20$ and $N_{\text{virt}} \cong 70$, which means that there are 588 million operations if no molecular symmetry is considered (C_1 point group).

In practice it is more efficient not to restrict the sum over $|K\rangle$ in Eq. (33) to test whether or not $|K\rangle$ belongs to S. The excess contributions can later be subtracted with much less computational effort.

Now we can carefully look at Eq. (34) where we go from $|I\rangle$ in S, to $|K\rangle \notin S$ and back to another determinant $|J\rangle$ in S. Diagrammatically, this means that since we took every $|I\rangle$ as a temporary vacuum state and we do not go back to it, the corresponding energy diagram will not be closed in the upper part.

The passage from $|I\rangle \in S$ to $|K\rangle \notin S$ and then to $|J\rangle \in S$ allows us to classify the diagrams in four types, since there are as many possibilities of excitation of $|J\rangle$ with respect to $|I\rangle$:

1) $|J\rangle$ is a mono-excited determinant with respect to $|I\rangle$.

2) $|J\rangle$ is a di-excited determinant with respect to $|I\rangle$.

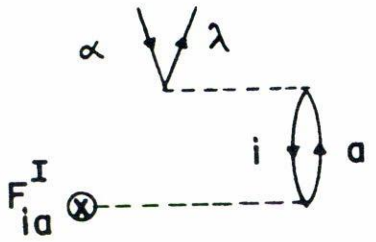
3) $|J\rangle$ is a tri-excited determinant with respect to $|I\rangle$.

4) $|J\rangle$ is a tetra-excited determinant with respect to $|I\rangle$.

We shall label the diagrams $nTmP$ meaning that $|J\rangle$ and $|K\rangle$ have n holes and m particles in common. This classification allows a more efficient programming. Occ and virt will mean that the sum over the corresponding index has to be over the occupied or virtual orbitals in $|I\rangle$ (the temporary vacuum).

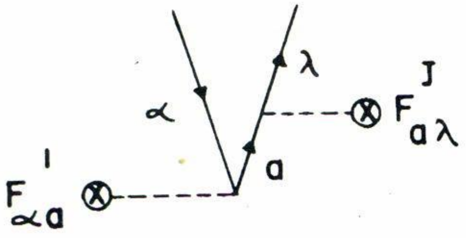
Let us start with the first case. The possibilities for $|K\rangle$ are only 2:

1.1) $|K\rangle$ is mono-excited with respect to $|I\rangle$
1.1.1) $1T1P$



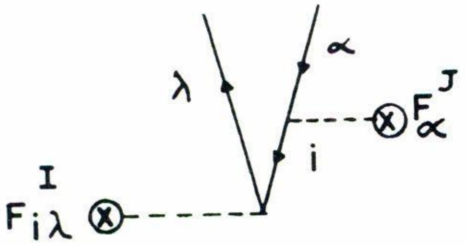
$$\sum_{i}^{\text{occ}}\sum_{a}^{\text{virt}}\frac{\langle\alpha a||\lambda i\rangle F^{I}_{ia}}{\varepsilon_a-\varepsilon_1}$$

1.1.2) $1P$



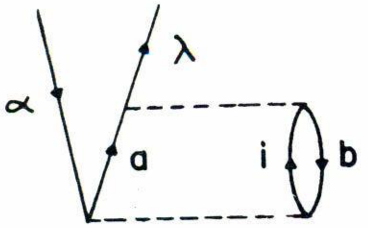
$$\sum_{a}^{\text{virt}}\frac{F^{J}_{a\lambda}F^{I}_{\alpha a}}{\varepsilon_a-\varepsilon_\alpha}$$

1.1.3) $1T$



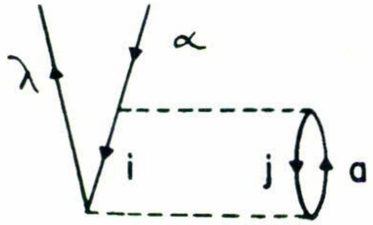
$$\sum_{i}^{\text{occ}}\frac{F^{J}_{\alpha i}F_{i\lambda}}{\varepsilon_\lambda-\varepsilon_i}$$

1.2) $|K\rangle$ is di-excited with respect to $|I\rangle$
1.2.1) $1T$



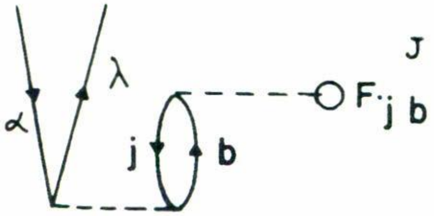
$$\sum_{a,b}^{\text{occ}}\sum_{i}^{\text{virt}}\frac{\langle\lambda i||ab\rangle\langle\alpha i||ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_i-\varepsilon_\alpha}$$

1.2.2) $1P$



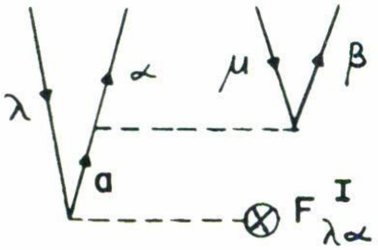
$$\sum_{a}^{\text{occ}}\sum_{i,j}^{\text{virt}}\frac{\langle ij\|\lambda a\rangle\langle a\alpha\|ji\rangle}{\varepsilon_a+\varepsilon_\lambda-\varepsilon_i-\varepsilon_j}$$

1.2.3) $1T1P$



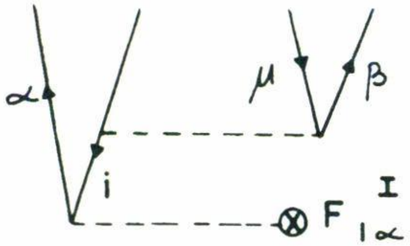
$$\sum_{b}^{\text{occ}}\sum_{j}^{\text{virt}}\frac{F^J_{jb}\langle j\alpha\|b\lambda\rangle}{\varepsilon_b+\varepsilon_\lambda-\varepsilon_j-\varepsilon_\alpha}$$

2) $|J\rangle$ is di-excited with respect to $|I\rangle$
2.1) $|K\rangle$ is mono-excited with respect to $|I\rangle$
2.1.1) $1T$



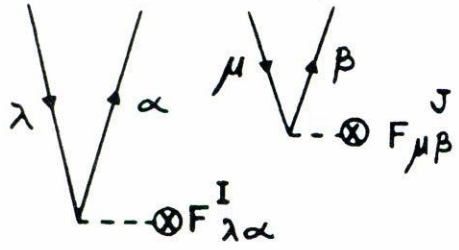
$$\sum_{a}^{\text{virt}}\frac{F^I_{\lambda a}\langle a\mu\|\alpha\beta\rangle}{\varepsilon_a-\varepsilon_\lambda}$$

2.1.2) $1P$



$$\sum_{i}^{\text{occ}}\frac{F^I_{i\alpha}\langle\lambda\mu\|i\beta\rangle}{\varepsilon_\alpha-\varepsilon_i}$$

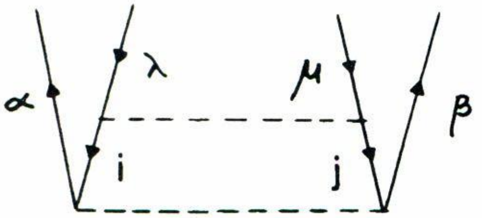
2.1.3) $1T1P$



$$\frac{F^J_{\mu\beta}F^I_{\lambda\alpha}}{\varepsilon_\alpha - \varepsilon_\lambda}$$

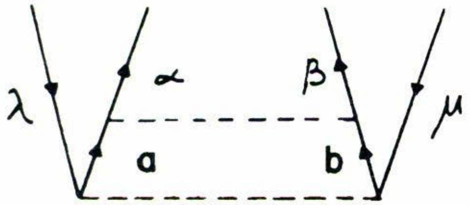
2.2) $|K\rangle$ is di-excited with respect to $|I\rangle$

2.2.1) $2T$



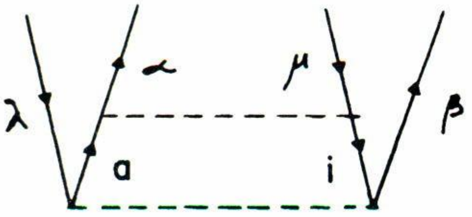
$$\sum_{i,j}^{\text{occ}} \frac{\langle\lambda\mu||ij\rangle\langle ij||\alpha\beta\rangle}{\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_i - \varepsilon_j}$$

2.2.2) $2P$



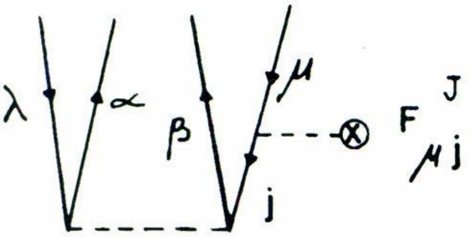
$$\sum_{a,b}^{\text{virt}} \frac{\langle ab||\alpha\beta\rangle\langle\lambda\mu||ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_\lambda - \varepsilon_\mu}$$

2.2.3) $1T1P$



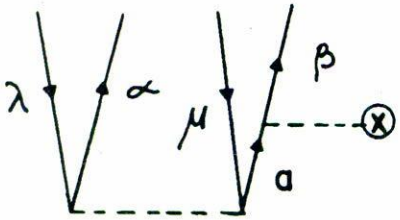
$$\sum_{a}^{\text{virt}}\sum_{i}^{\text{occ}} \frac{\langle a\mu||\alpha i\rangle\langle\lambda i||a\beta\rangle}{\varepsilon_a + \varepsilon_\beta - \varepsilon_\lambda - \varepsilon_i}$$

2.2.4) $1T2P$



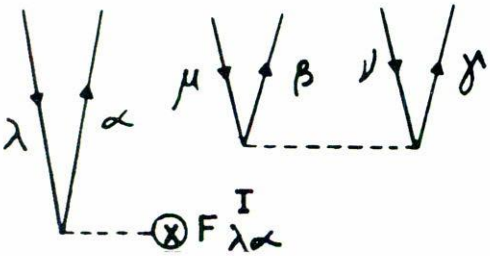
$$\sum_{j}^{\mathrm{occ}} \frac{F^{J}_{\mu j}\langle \lambda j \| \alpha\beta\rangle}{\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_\lambda - \varepsilon_j}$$

2.2.5) $2T1P$



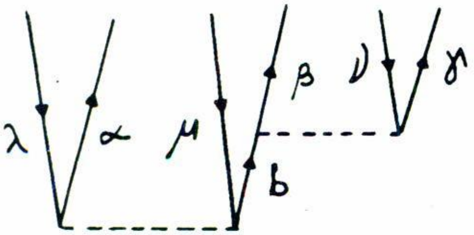
$$\sum_{a}^{\mathrm{virt}} \frac{F^{J}_{a\beta}\langle \lambda\mu \| \alpha a\rangle}{\varepsilon_\alpha - \varepsilon_a - \varepsilon_\lambda - \varepsilon_m u}$$

3) $|J\rangle$ is tri-excited with respect to $|I\rangle$
3.1) $|K\rangle$ is mono-excited with respect to $|I\rangle$
3.1.1) $1T1P$



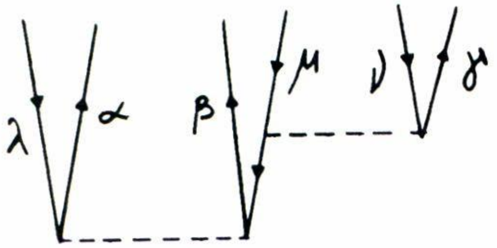
$$\frac{F^{I}_{\lambda\alpha}\langle \mu\nu \| \beta\gamma\rangle}{\varepsilon_\alpha - \varepsilon_\lambda}$$

3.2) $|K\rangle$ is di-excited with respect to $|I\rangle$
3.2.1) $2T1P$



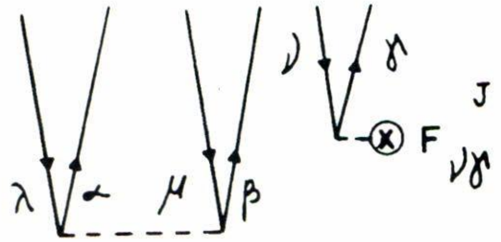
$$\sum_{b}^{\mathrm{virt}} \frac{\langle \lambda\mu \| \alpha b\rangle\langle b\nu \| \beta\gamma\rangle}{\varepsilon_b + \varepsilon_\alpha - \varepsilon_\lambda - \varepsilon_\mu}$$

3.2.2) $1T2P$



$$\sum_{i}^{\text{occ}} \frac{\langle \lambda i|\alpha\beta\rangle\langle\mu\nu||i\gamma\rangle}{\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_\lambda-\varepsilon_i}$$

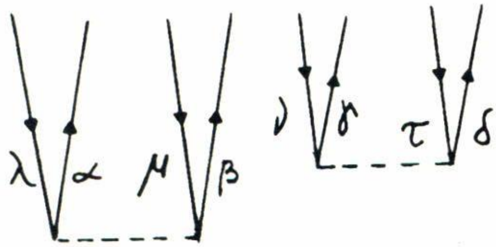
3.2.3) $2T2P$



$$\frac{F^J_{\nu\gamma}\langle\lambda\mu||\alpha\beta\rangle}{\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_\lambda-\varepsilon_\mu}$$

4) $|J\rangle$ is tetra-excited with respect to $|I\rangle$

4.1) Because of the bi-electronic nature of the perturbation, $|K\rangle$ can only be a di-excited determinant with respect to $|I\rangle$



$$\frac{\langle\lambda\mu||\alpha\beta\rangle\langle\nu\tau||\gamma\delta\rangle}{\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_\lambda-\varepsilon_\mu}$$

This set of diagrams encompasses all the possible connections between $|I\rangle$ and $|J\rangle$, both in the reference space S.

In practice, a set of arrays has to be constructed specifying which orbitals are occupied and virtual for each determinant in S, so that the constraint $|K\rangle \notin S$ can be met.

It should be said that this way of generating determinants $|K\rangle$ connecting $|I\rangle$ and $|J\rangle$ can produce a given determinant $|K_o\rangle$ several times for many different couples $|I\rangle, |J\rangle$. For this reason it is not possible to count or keep track of the most important (those having the largest perturbative coefficient) determinants $|K\rangle$ generated in the perturbational space P. This is why we cannot follow the original iterative technique of the non-diagrammatic CIPSI algorithm. In the standard version of CIPSI, determinants in P having a coefficient larger than a given threshold could be introduced in S to improve the zeroth order description of a given state and generate more determinants in P. Therefore,

System	Number electrons	of M.O.	NCF	NPERT $\times 10^6$	CIPSI	CIPDIAG
CuCl	18	45	494	14	73 h	2 h 10 min
CuI	18	61	372	23	2 h 43 min*	4 min 30 s*
Ar_4^+	31	68	56	6.5	5 h 14 min	14 min
Cu	11	32	261	10	14 h 30 min	2 h 37 min
Na_9^+	8	50	374	10	19 h 20 min	2 h 5 min
Pb_2H_4	12	46	58	1	1 h 10 min	10 min

TABLE I. CPU times on a μVAX-II for the standard (CIPSI) and its diagrammatic version (CIPDIAG). *On the Fujitsu Vector Processor VP-200.

the faster diagrammatic approach is useful when one has already determined the final reference space using the standard CIPSI program.

Table I shows CPU times on a μVAX-II for both algorithms, the standard CIPSI program and the diagrammatic version of it, CIPDIAG. A a variety of systems was studied with different number of electrons, of molecular orbitals and with different number (NCF) and types of determinants in the reference space. The number of determinants (NPERT) in the perturbational spaces was obtained using the standard CIPSI program.

We can see a very large range of relative speeds, CIPDIAG being 6 to 40 times faster than the standard version. This large variation stems from the different types of reference spaces needed for each case. In order to overcome the difficulty of resetting the particle-hole array from $|O\rangle$ (the closed shell Hartree-Fock $|\Phi_0\rangle$ reference) to the one corresponding to each determinant $|I\rangle$ in S, we propose to hierarchically arrange (mono, di, tri, tetra-excitations with respect to $|O\rangle$) the reference space and make only minor changes to this array as the $|I\rangle$ index evolves.

CONCLUSION

This is a review article devoted to explain in simple terms what the power of the diagrammatic technique can do for a highly computational problem as the one posed by the second order perturbational energy for a zeroth order multireference wave function.

It is important to highlight the advantages of such a size-consistent method in contrast to others like the MCSCF or MRSDCI that also aim at treating electronic correlation but fail to yield as accurate results when size-consistence plays a role (*i.e.*, the dissociation energy for a typical reaction like $HCuCH_3 \rightarrow Cu + CH_4$ is wrong by tens of Kcal/mol even with large MRCI calculations using MCSCF molecular orbitals for the state under study). Of course the Coupled Cluster methods (which are size-consistent by construction) like the CCSD-T1 or CCSD + T(CCSD) yield nowadays excellent values for many molecular properties but fail again when a single reference wave function cannot account for the breaking of bonds. One must then resort to the recently implemented Multi-Reference CC methods [25] but here the problem becomes a practical one. These MRCC algorithms are a lot more time and space consuming than the present diagrammatic MP2 program. So, when one does not have unlimited amounts of time and memory in a fast computer, one can very easily resort to the present algorithm and yet obtain highly accurate and reliable results for molecular systems having 20–50 valence electrons and monoelectronic bases ranging from 50 to 120 molecular orbitals.

REFERENCES

1. H.J. Silverstone and O. Sinanoğlu. *J. Chem. Phys.* **44** (1966) 1899.
2. K. Wolinski, H.L. Sellers and P. Pulay, *Chem. Phys. Lett.* **140** (1987) 225.
3. C. Möller and M.S. Plesset, *Phys. Rev.* **46** (1934) 618.
4. P.O. Löwdin, *J. Math. Phys.* **6** (1965) 1341.
5. F. Dupont-Bourdelet, J. Tillien and J. Guy, *J. Phys. Radium* **21** (1960) 776.
6. K.A. Brueckner, *Phys. Rev.* **100** (1955) 36.
7. P. Claverie, S. Diner and J.P. Malrieu, *Int. J. Quant. Chem.* **1** (1967) 751.
8. H.P. Kelly, *Adv. Chem. Phys.* **XIV** (1969) 129.
9. R.P. Feynman, "The development of the space-time view of quantum electrodynamics", *Science* **153** (1966) 699.
10. J. Goldstone, *Proc. Roy. Soc. London A.* **239** (1957) 267.
11. H.P. Kelly, *Phys. Rev.* **131** (1963) 684; **144** (1966) 39.
12. K.F. Freed, *Ann. Rev. Phys. Chem.* **21** (1972) 313.
13. J. Paldus and J. Čizek, *Adv. Quant. Chem.* **9** (1975) 105.
14. I. Hubac and P. Carsky, *Topics Current. Chem.* **75** (1978) 97.
15. I. Lindgren and J. Morrison, *Atomic Many Body Theory*, Springer-Verlag, Berlin (1982).
16. S. Wilson, *Computer Phys. Rep.* **2** (1985) 389.
17. J.L. Whitten and M. Hackenmayer, *J. Chem. Phys.* **51** (1969) 5584.
18. R.J. Buenker and S.D. Peyerimhoff, *Theoret. Chim.* **35** (1974) 33; **39** (1975) 217.
19. R.J. Buenker, S.D. Peyerimhoff and W. Butscher, *Mol. Phys.* **35** (1978) 771.
20. B. Huron, P. Rancurel and J.P. Malrieu, *J. Chem. Phys.* **58** (1973) 5745.
21. S. Evangelisti, J.P. Daudey and J.P. Malrieu, *Chem. Phys.* **75** (1983) 91.
22. J.P. Malrieu and F. Spiegelmann, *Theoret. Chim. Acta (Berl.)* **52** (1979) 55.
23. R. Cimiraglia, *J. Chem. Phys.* **83** (1985) 1746.
24. R. Cimiraglia and M. Persico, *J. Comput. Chem.* **8** (1987) 39.
25. I. Lindgren, *Int. J. Quant. Chem. Symp.* **12** (1978) 33; W.D. Laidig and R.J. Bartlett, *Chem. Phys. Lett.* **104** (1984) 424; I. Lindgren and D. Mukherjee, *Phys. Rev.* *A***151**(1987) 93.