

Iterative perturbation calculations of ground and excited state energies from multiconfigurational zeroth-order wavefunctions

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Iterative perturbation calculations of ground and excited state energies from multiconfigurational zeroth-order wavefunctions

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A method is proposed to calculate the effect of configuration interaction by a Rayleigh-Schrödinger perturbation expansion when starting from a multiconfigurational wavefunction. It is shown that a careless choice of H_0 may lead to absurd transition energies between two states, at the first orders of the perturbation, even when the perturbation converges for both states. A barycentric definition of H_0 is proposed, which ensures the cancellation of common diagrams in the calculated transition energies. A practical iterative procedure is defined which allows a progressive improvement of the unperturbed wavefunction ψ^0 ; the CI matrix restricted to a subspace S of strongly interacting determinants is diagonalized. The desired eigenvector ψ^0 of this matrix is perturbed by the determinants which do not belong to S . The most important determinants in ψ^1 are added to S , etc. The energy thus obtained after the second-order correction is compared with the ordinary perturbation series where ψ^0 is a single determinant. For the ground state, this procedure includes, besides the whole second-order correction, the most important terms of the third and fourth orders. The question of orthogonality of excited states is discussed. This technique, hereafter called CIPSI, has been tested on the ground and several excited states of H_2 , Ne, and MgO, showing both a rapid convergence of the calculated transition energy and the importance of correlation effects on transition energy.

INTRODUCTION

The use of a perturbation technique for the study of correlation corrections to various observables has been suggested almost immediately after the Hartree-Fock approximation.¹ The many-body problem theories brought to this fundamental idea a set of powerful techniques—second quantization formalism, diagrammatic representations—and very important results, among which one may quote essentially the superiority of the Rayleigh-Schrödinger over the Brillouin perturbation expansion,² the linked cluster theorem,³ and various infinite summations of partial series.^{2,4}

These methods were initially applied to the electron gas and the nucleus. In a more or less elaborate way, they have been applied to the atom by Kirginitz,⁵ Kelly,⁶ and Tolmachev,⁷ and some diatomic molecules by Grimaldi⁸ and Schulman and Kaufman⁹ for the ground state energy calculation. The analogous *ab initio* calculations on polyatomic systems are rare,^{10,11} but these techniques have received several applications for semiempirical calculations on polyatomic systems.¹² Analogous methods may be employed for the calculation of other ground state observables, especially magnetic properties, transition probabilities, polarizabilities, and scattering properties (Kelly,¹³ Das,¹⁴ Sandars¹⁵).

The perturbative methods are especially attractive

for their speed and the interpretative nature of their results in terms of contributions of "physical" processes.

At the present stage the method is essentially applied to the cases where the zeroth-order wavefunction is a single determinant. Some extensions of the method have been proposed by Sandars¹⁵ and Tolmachev¹⁶ to treat states with a zeroth-order wavefunction that must be represented as a linear combination of degenerated determinants. It is actually possible to establish a simple diagrammatic representation of the perturbation series for an excited singlet (or triplet) state $\psi_{pq^*}^1$ (or 3) built from a closed shell system Φ_0 by a single excitation pq^* (the asterisked orbitals represent virtual, vacant orbitals for the reference ground state Φ_0):

$$\psi_{pq^*}^1 \text{ (or } ^3) = 1/\sqrt{2} (a^+_{q^*} a_p (\pm) a^+_{\bar{q}} a_{\bar{p}}) \Phi_0.$$

This case is a case of spin degeneracy. The treatment of spatial full degeneracy does not present more difficulty.

It is more difficult to treat the cases where one cannot find a satisfactory zeroth-order wavefunction in the form of a single determinant or a linear combination of *degenerate* single determinants. This may occur even for a "closed-shell" system when several determinants interact strongly; one may quote as an

example the ground state of MgO for which the SCF calculation leads to several singly and doubly excited determinants with a low energy above the SCF Φ_0 .¹⁷ The same thing occurs for polyatomic systems when chemical bonds are broken in the course of a reaction or of a rotation.¹⁸ In such cases some excited determinants

$$\Phi = a_i^+ a_j^+ a_k a_l \Phi_0$$

have a large matrix element with Φ_0 compared with the energy difference $E_0 - E_\Phi$. Then if the ratio $\langle \Phi | H | \Phi_0 \rangle / (\epsilon_k + \epsilon_l - \epsilon_i - \epsilon_j)$ is too large, the series diverge or converge too slowly to give significant and reliable results at the first orders. This is the field of applications of the multiconfiguration self-consistent methods (MCSCF). But in the present stage, the MCSCF methods applied to rather large molecules only include a small number of determinants and give a poor part of the correlation energy.¹⁹ Therefore it could be worthwhile to evaluate most of the remaining part of the correlation energy by a perturbational treatment on the MCSCF wavefunction. The first purpose of that paper is to propose and discuss a possible procedure to perform such a perturbation.

The same problem of course exists for most of the excited states. Most of the excited states wavefunctions represented by a linear combination of determinants with the same space part—say a singly excited configuration Φ_{pq^*} —present near degeneracy with other singly excited states Φ_{rs^*} or with low-lying doubly excited configurations. For instance the interaction of the first $\pi\pi^*$ singlet configuration in the ethylene molecule is strongly mixed with the lowest $\sigma\sigma^*$ singlet configuration.²⁰ Our second purpose is to find a procedure to calculate the nearly degenerate excited state energies by a perturbation calculation of the correlation effects after a preliminary variational mixture of the strongly interacting configurations. This paper discusses the difficulty in obtaining significant transition energies at the first orders of perturbation for large systems by perturbing two states which are approximated by linear combinations of nearly degenerate determinants, and suggests a definition of the unperturbed Hamiltonian H_0 for which the cancellation of common diagrams in the transition energy²¹ still occurs.

I. CHOICE OF THE UNPERTURBED HAMILTONIAN

A. Definitions of the Unperturbed Hamiltonian for the Nondegenerate Cases

To define the unperturbed Hamiltonian H_0 as the Hartree-Fock operator for the considered n -electron systems in a state Φ_0 , one uses

$$H_0 = \sum_i h(i) + C, \quad (1)$$

where

$$h(i) = -\frac{1}{2}\nabla^2(i) + T(i) + \sum_j J_j(i) - K_j(i)$$

is the mono-electronic HF operator and C is a constant. Then Φ_0 and all the other determinants built from the eigenvectors of $h(i)$,

$$h\psi_i = \epsilon_i \psi_i, \quad (2)$$

are eigenvectors of H_0 . The constant C is often chosen to satisfy the following relationships:

$$H_0 \Phi_0 = E_0 \Phi_0, \quad (3)$$

$$E_0 = \langle \Phi_0 | H | \Phi_0 \rangle, \quad (4)$$

where H is the exact Hamiltonian. Then in the second quantization formalism H_0 may be written as

$$H_0 = \sum_i \epsilon_i a_i^+ a_i + C. \quad (5)$$

The fundamental results of the many-body perturbation theory (definition of the diagrammatic series, linked cluster theorem, ...) are only valid if the unperturbed Hamiltonian is a simple sum of mono-electronic operators. We call this partition of the total Hamiltonian¹ Moller-Plesset.

Another important result appears with such a definition of H_0 , namely the cancellation of common diagrams in the calculation of transition energies.²¹ Let us suppose that one is interested in the energy difference between a closed-shell ground state Φ_0 and a singly excited, $S_s=1$, triplet state which may be represented as a first approximation by the single determinant,

$$| \Phi_{pq^*} \rangle = a^+ a^+ a_p^- | \Phi_0 \rangle. \quad (6)$$

These two states, both eigenvectors of H_0 , may be perturbed by the "correlation operator" $V = H - H_0$. Although these two states do not define the same vacuum state, most of the diagrams of the energy (all those which do not imply the mono-electronic functions p and q^* involved in the zeroth-order description of the transition process $| \Phi_0 \rangle \rightarrow | \Phi_{pq^*} \rangle$) are identical in both series and cancel in the calculation of the transition energy.

It had been noticed from the beginning by Brueckner² that certain kinds of ladder diagrams may be summed up at all orders of the perturbation series and that this summation simply leads to a new definition of the denominators in the perturbation series. If E_I is the eigenvalue of H_0 corresponding to any determinant $\Phi_I \neq \Phi_0$,

$$H_0 \Phi_I = E_I \Phi_I; \quad (7)$$

then, the denominator $(E_0 - E_I)$ becomes $\langle 0 | H | 0 \rangle - \langle I | H | I \rangle$. This procedure, which significantly im-

proves the order results, has been widely used by Kelly on the atom.¹³ This procedure is simply equivalent to a different partition of the total Hamiltonian H into a diagonal unperturbed Hamiltonian H_0' and a zero-diagonal perturbation operator V' ,²² i.e., $H = H_0' + V'$,

$$\begin{aligned} H_0' | \Phi_I \rangle &= \langle \Phi_I | H | \Phi_I \rangle | \Phi_I \rangle = E_I' | \Phi_I \rangle \\ \langle \Phi_I | V' | \Phi_I \rangle &= 0. \end{aligned} \tag{8}$$

H_0' has the same set of eigenvectors as H_0 , but different eigenvalues, and is no longer a sum of mono-electric operators. This partition, which may be called Epstein-Nesbet according to its earlier applications,²³ is widely used now,¹⁰ but the diagrammatic expansion and the related results are not valid in this H_0' perturbation series. It is worthwhile to come back to the H_0 series and its properties before summing up the diagrams which give the corresponding results in the H_0' series.

B. Change of the CI Basis Set for the Nearly Degenerate Case

In our case, we do not want to treat as a perturbation the direct interaction between a certain number of determinants belonging to a given subspace S of the total vectorial space of the N electron determinants. When all these determinants have the same energy (full degeneracy), the classical treatments for degenerate systems hold.

At the end of the MCSCF procedure, for instance, one performs a diagonalization of a CI matrix limited to a set S of determinants. It gives a set of vectors, linear combinations of these determinants, but the virtual orbitals obtained also allow building of de-

terminants outside of S . Even if we do not perform a variational optimization of the MO's, our procedure will imply a preliminary diagonalization of the CI restricted to the subspace S of strong interaction. If P_s is the projector on the subspace S , one seeks the eigenvectors of $P_s H P_s$,

$$P_s H P_s | \psi_m \rangle = \epsilon_m | \psi_m \rangle. \tag{9}$$

The eigenvalues ϵ_m of this limited CI are the mean value energies of the linear combinations of determinants $|\psi_m\rangle$,

$$\epsilon_m = \langle \psi_m | H | \psi_m \rangle. \tag{10}$$

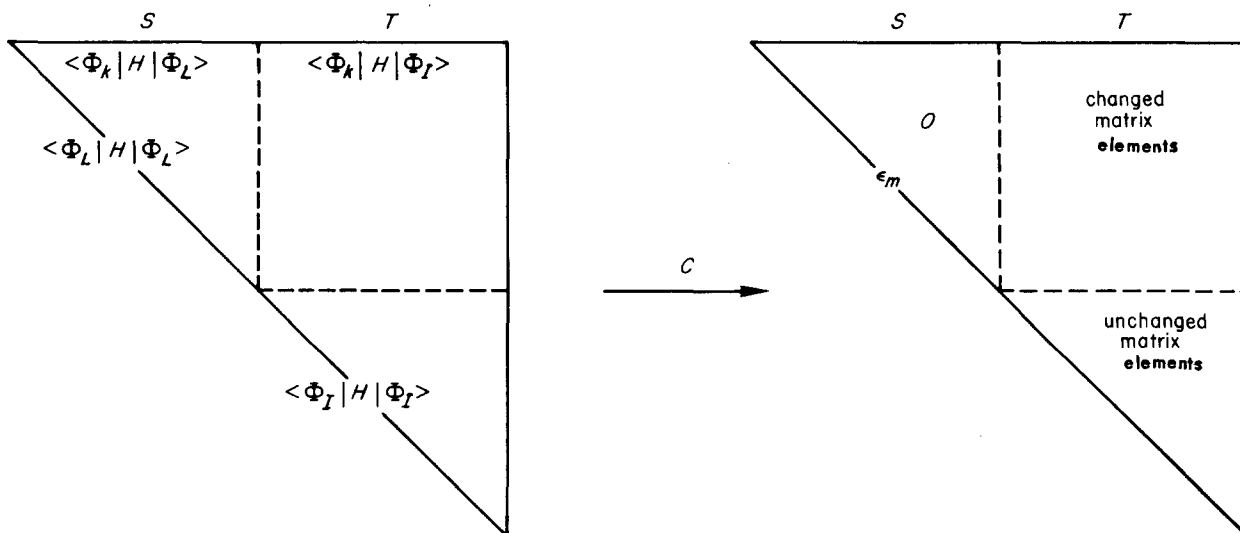
This diagonalization of $P_s H P_s$ leads to a unitary change of the basis of the vectorial space S , from the Φ_k 's to the ψ_m 's; the "complete" basis set of determinants may be transformed into another "complete" basis set, built from the ψ_m in the subspace S and from the unchanged determinants Φ_I in the subspace T complementary to S . If C_s is the unitary matrix allowing the transformation from the $\Phi_k \in S$ into the ψ_m ,

$$\psi_m = \sum_{k \in S} C_{m,k} \Phi_k, \tag{11}$$

the final transformation $C = C_s \otimes I_T$ of the basis set may be visualized as follows:

$$\begin{array}{l} C_S \\ S, \Phi_K \longrightarrow \psi_m, \\ \\ I_T \\ T, \Phi_I \longrightarrow \Phi_I, \end{array}$$

and the Hamiltonian constructed in this new basis possesses a diagonal bloc in the subspace S .



If the subspace S has been correctly chosen, no near degeneracy appears between the lowest eigenvectors ψ_m and any other vector of the new basis set, since $\langle \psi_m | H | \psi_n \rangle = 0$ for all ψ_n belonging to S , and $\epsilon_m - \langle \Phi_i | H | \Phi_i \rangle$ is very large if S includes enough vectors. For instance S may include all singly excited determinants of a given symmetry. The lowest energy eigenvectors of $P_0 H P_0$ are then well separated from the lowest doubly excited determinants. Then one may take the lowest vectors ψ_m as unperturbed zeroth-order wavefunction $\psi^0 = \psi_m$ as proposed by Gershgorin and Shavitt.²⁴ In this new basis the main problem is the choice of the H_0 Hamiltonian.

C. Inadequacy of a Generalized Epstein-Nesbet Definition of H_0

One might try, as a natural procedure, to extend the Epstein-Nesbet partition defined previously,

$$H_0' | \psi_m \rangle = \epsilon_m | \psi_m \rangle, \tag{12}$$

$$H_0' | \Phi_I \rangle = \langle \Phi_I | H | \Phi_I \rangle | \Phi_I \rangle, \quad \text{if } I \in T. \tag{13}$$

This is the solution adopted by Gershgorin and Shavitt.²⁴ We want to demonstrate here that such a definition of H_0' would lead to absurd results on large enough systems.

Let us consider a model problem of $(n+2)$ molecules of hydrogen, two of them interacting strongly, the others being far apart from each other. This problem is, of course, the limiting case of any molecular problem where the interaction between the two-electron bonds is considered as negligible. Then, if ϕ_i is the lowest molecular orbital for each molecule i , for instance an SCF localized MO, the ground state determinant of the $(n+2)$ electron system may be written

$$\Phi_0 = | \phi_1 \bar{\phi}_1 \cdots \phi_n \bar{\phi}_n \phi_{n+1} \bar{\phi}_{n+1} \phi_{n+2} \bar{\phi}_{n+2} |. \tag{14}$$

Let us consider on the other hand a triplet $S_z = 1$ excited state built from singly excited determinants on the two last, strongly interacting molecules, $n+1$ and $n+2$.

One may consider two locally excited triplets,

$$\Phi_1 = | \phi_1 \bar{\phi}_1 \phi_n \bar{\phi}_n \phi_{n+1} \phi_{n+1}^* \phi_{n+2} \bar{\phi}_{n+2} |$$

and

$$\Phi_2 = | \phi_1 \bar{\phi}_1 \phi_n \bar{\phi}_n \phi_{n+1} \bar{\phi}_{n+1} \phi_{n+2} \phi_{n+2}^* |, \tag{15}$$

where ϕ_{n+1}^* and ϕ_{n+2}^* are, for instance, the lowest vacant MO's localized on the molecules $n+1$ and $n+2$. The CI between these two determinants defining S will lead to two eigenvectors ψ_1 and ψ_2 and two eigenvalues ϵ_1 and ϵ_2 . Let us assume that the two molecules are in a symmetrical position; let us call E the mean value energy relative to Φ_1 and Φ_2 ,

$$E - E_0 = \langle \Phi_1 | H - E_0 | \Phi_1 \rangle = \langle \Phi_2 | H - E_0 | \Phi_2 \rangle = \epsilon_{n+1}^* - \epsilon_{n+1} - J_{n+1, n+1}^*, \tag{16}$$

and b the interaction matrix element,

$$b = \langle \Phi_1 | H | \Phi_2 \rangle = \langle \phi_{n+1}^{*(1)} \phi_{n+2}^{(2)} | (1/r_{12}) | \phi_{n+2}^{*(1)} \phi_{n+1}^{(2)} \rangle. \tag{17}$$

Then

$$\begin{aligned} \epsilon_1 &= E - b, & \psi_1 &= (\Phi_1 + \Phi_2) / \sqrt{2}, \\ \epsilon_2 &= E + b, & \psi_2 &= (\Phi_1 - \Phi_2) / \sqrt{2}. \end{aligned} \tag{18}$$

Let us perturb successively the three wavefunctions Φ_0 , ψ_1 , and ψ_2 to the second order in energy. For Φ_0 one will find the interaction with all the diexcited determinants, and the leading terms will come from the diexcitations from the n isolated two-electron systems.

Let us call

$$\Phi \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix}$$

the diexcited determinant,

$$\left| \Phi \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} \right\rangle = a^+_{i^*} a^+_{\bar{i}'^*} a_{i'} a_i | 0 \rangle. \tag{19}$$

Then the second-order correlation energy resulting from the diexcitations from the molecule i is given by

$$e_{i,0}^2 = \sum_{i^* \bar{i}'^*} \left\{ \left| \langle \Phi_0 | H | \Phi \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} \rangle \right|^2 / \left[E_0 - E \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} \right] \right\}. \tag{20}$$

This expression may be transformed into

$$e_{i,0}^2 = \sum_{i^* \bar{i}'^*} \sum_{i' i} \langle \phi_i \phi_i | r_{12}^{-1} | \phi_{i^*} \phi_{\bar{i}'^*} \rangle^2 \left[\Delta E \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} \right]^{-1}. \tag{21}$$

The total second-order energy is equal to

$$e_0^2 = \sum_i e_{i,0}^2 + d_0 = n e_{i,0}^2 + d_0,$$

where d_0 is a correction resulting from the excitations on molecules $n+1$ and $n+2$. All the intermolecular diexcitations involving the molecules $i = 1-n$ give zero corrections if the n molecules are separated enough.

Now let us perturb ψ_1 or ψ_2 . We must consider all the triexcited configurations obtained from ψ_1 or ψ_2 by diexcitations on the systems i ,

$$\begin{aligned} \Phi_a &= \left| \Phi \begin{pmatrix} (n+1)_\alpha^* & i & \bar{i}'^* \\ (n+1)_\beta & i & \bar{i} \end{pmatrix} \right\rangle = a^+_{i^*} a^+_{\bar{i}'} a_i | \Phi_1 \rangle, \\ \Phi_b &= \left| \Phi \begin{pmatrix} (n+2)^* & i & \bar{i}'^* \\ (n+2)_\beta & i & \bar{i} \end{pmatrix} \right\rangle = a^+_{i^*} a^+_{\bar{i}'} a_i | \Phi_2 \rangle, \end{aligned}$$

$$\begin{aligned} \langle \psi_1 | H | \Phi_a \rangle &= \langle \Phi_1 | H | \Phi_a \rangle / \sqrt{2} = \langle \phi_i \phi_i | r_{12}^{-1} | \phi_i^* \phi_i^* \rangle / \sqrt{2}, \\ \langle \psi_2 | H | \Phi_b \rangle &= \langle \Phi_2 | H | \Phi_b \rangle / \sqrt{2} = \langle \phi_i \phi_i | r_{12}^{-1} | \phi_i^* \phi_i^* \rangle / \sqrt{2}, \end{aligned} \tag{22}$$

where α and β subscripts indicate α and β spins.

The corresponding energy denominators appearing in the second-order perturbation corrections are

$$\Delta E' = \langle \psi_1 | H | \psi_1 \rangle - \langle \Phi_a | H | \Phi_a \rangle = \langle \psi_1 | H | \psi_1 \rangle - \langle \Phi_b | H | \Phi_b \rangle. \tag{23}$$

Using the general formulas for single determinant transition energies,²⁵ and neglecting the Coulombic integrals between different systems, one obtains

$$\langle \psi_1 | H | \psi_1 \rangle - \langle \Phi_a | H | \Phi_a \rangle = \Delta E \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} - b. \tag{24}$$

The excitations

$$\begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix}$$

on Φ_1 and Φ_2 lead to a second-order correction on ψ_1 ,

$$e_{i,1}^2 = \sum_{i^*} \sum_{\bar{i}'^*} \langle \phi_i \phi_i | r_{12}^{-1} | \phi_i^* \phi_i^* \rangle \left[\Delta E \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} - b \right]^{-1}, \tag{25}$$

as all the denominators appearing in $e_{i,1}^2$ are larger (in absolute value) than the corresponding quantities in $e_{i,0}^2$, $|e_{i,1}^2| < |e_{i,0}^2|$. On the contrary in $e_{i,2}^2$, corresponding to the perturbation of ψ_2 , the denominators are

$$\left[\Delta E \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} + b \right]$$

and $|e_{i,2}^2| > |e_{i,0}^2|$. Let us make a closure approximation on the diexcitation energies

$$\Delta E \begin{pmatrix} i^* & \bar{i}'^* \\ i & \bar{i} \end{pmatrix} = \Delta E$$

or assume that only one diexcitation is efficient for each system i . Then

$$\begin{aligned} e_{i,1}^2 &= e_{i,0}^2 (1 - b/\Delta E)^{-1}, \\ e_{i,2}^2 &= e_{i,0}^2 (1 + b/\Delta E)^{-1}. \end{aligned} \tag{26}$$

Now summing the contributions of all the systems i , one gets as total second-order correction for ψ_1 ,

$$\begin{aligned} e_1^2 &= \sum_i e_{i,1}^2 + d_1 = n e_0^2 (1 - b/\Delta E)^{-1} + d_1, \\ e_1^2 &= n e_{i,0}^2 (1 - b/\Delta E)^{-1} + d_1, \end{aligned}$$

and for ψ_2 ,

$$e_2^2 = n e_{i,0}^2 (1 + b/\Delta E)^{-1} + d_2, \tag{27}$$

where d_1 and d_2 are some specific corrections arising from excitations on the systems $n+1$ and $n+2$. Then the second-order correction to the transition energy is equal to

$$\begin{aligned} e_{T_1}^2 &= e_1^2 - e_0^2 = d_1 - d_0 + n e_{i,0}^2 [(1 - b/\Delta E)^{-1} - 1], \\ e_{T_1}^2 &\simeq d_1 - d_0 + n e_{i,0}^2 b/\Delta E, \\ e_{T_2}^2 &\simeq d_2 - d_0 - n e_{i,0}^2 b/\Delta E. \end{aligned} \tag{28}$$

As b is supposed to be positive and ΔE and e_0^2 are negative, the second-order correction to the transition energy of the lowest state ψ_1 increases proportionally to n , number of noninteracting systems, while the second-order correction to the second transition energy (of ψ_2) diminishes linearly with n . For large enough n , one will get negative transition energies toward ψ_2 ! This result is, of course, meaningless; the n molecules we introduced artificially at infinite distances should not influence the transition energy on the system ($n+1$, $n+2$). The n dependency of the transition energy is due to the choice of the denominators, i.e., to a bad choice of H_0 .

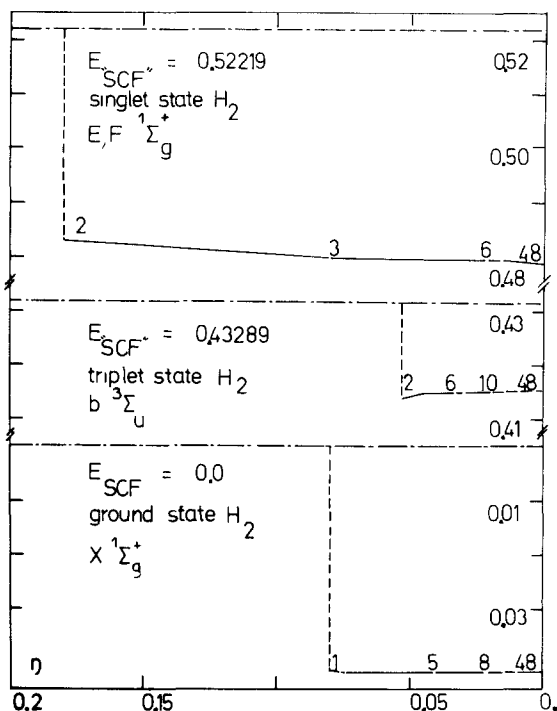


FIG. 1. Evolution of the second-order corrected energies of the $X^1\Sigma_g^+$, $b^3\Sigma_u$, and $E, F^1\Sigma_g^+$ states of H_2 as a function of η (amplitude of the largest coefficient in Ψ^1). The exact solution is for $\eta=0$. The "SCF" energies are the energies of the Ψ^0 wavefunctions built with the minimal number of determinants to get the symmetry properties, using the SCF MO's of the ground state problem. All energies are in atomic units. The numbers on the curves represent the number of determinants in Ψ^0 for the considered calculation.

This example is a very simple model demonstrating that at a given (low) order of perturbation a bad choice of H_0 may lead to absurd results on the transition energies between two states, even when the perturbation expansion converges for both states. Our model problem is not as artificial as it might seem; one may consider a more realistic problem, for instance the treatment of the transition energy of a butadiene molecule substituted by a long saturated chain, starting from localized molecular orbitals. The $\pi\pi^*$ excited state zeroth-order wavefunction may be written as a linear combination of singly $\pi\pi^*$ excited states. The development follows the same features as our model problem; the only changes concern the introduction of the interbond diexcitations and some Coulomb integrals $J_{\pi\sigma}$ between the π MO's and distant σ orbitals. The same conclusion holds for the same problem when one uses π delocalized MO's, if the excited state zeroth-order wavefunction results from the CI of the two $\pi\pi^*$ excited states of the same symmetry $\psi_1 = \lambda(\pi_2 \rightarrow \pi_3^*) + \mu(\pi_1 \rightarrow \pi_4^*)$.

D. Definition and Properties of the "Barycentric" H_0

Therefore it is impossible to use the Epstein-Nesbet definition of the unperturbed Hamiltonian H_0 for the

calculation of the transition energy between two states when one of the states is represented at the zeroth order by a linear combination of nondegenerate determinants.

Let us come back then to the Moller-Plesset definition of H_0 . Let us write

$$H_0' |\psi_m\rangle = \langle \psi_m | H_0 | \psi_m \rangle |\psi_m\rangle,$$

where H_0 is the classical HF n -electron Hamiltonian. The new eigenvalue corresponding to ψ_m , ϵ_m' is the barycenter of the single determinant eigenvalues for ψ_m ,

$$\epsilon_m' = \langle \psi_m | H | \psi_m \rangle = \sum_{i \in S} c_{m,i}^2 \langle \Phi_i | H_0 | \Phi_i \rangle,$$

since H_0 is diagonal in the basis of determinants. Then one may demonstrate that the processes which are possible on two different zeroth-order states (even when they are linear combinations of determinants) cancel in the calculation of the transition energy between the two states, and the absurd result previously noticed with the Epstein-Nesbet definition of H_0 no longer occurs.

Let us consider for instance a nondegenerate ground state approximation Φ_0 and a zeroth-order wavefunction ψ_m for an excited state,

$$|\psi_m\rangle = \sum_{i \in S} C_{m,i} |I\rangle.$$

Let us consider a diexcitation process D^+ , which may act on Φ_0 and all the configurations Φ_I belonging to S , without giving zero. Then if $D^+ = a_i^+ a_j^+ a_k a_l$, the cor-

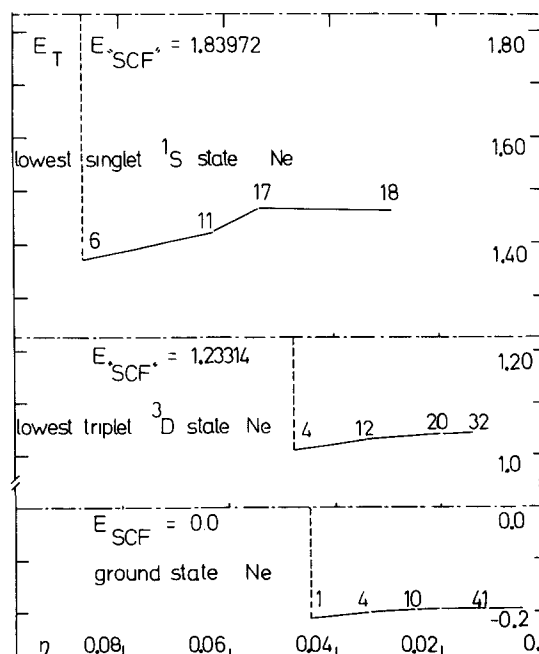


FIG. 2. Detailed evolution of the second-order corrected energy of the $X^1\Sigma_g^+$ state of H_2 as a function of η .

TABLE I. Convergence of the iterative perturbational process for the ground state of H₂ (all energies in atomic units).

ncf^a	1	2	4	5	8	13	21	48
E_D^b	0.0	-0.005340	-0.017593	-0.025167	-0.032769	-0.037509	-0.040032	-0.042796
E_T^c	-0.042911	-0.044268	-0.044501	-0.043925	-0.043333	-0.043083	-0.042897	-0.042796
% of E_{corr}^d	100.26	103.43	103.98	102.63	101.25	100.67	100.23	1.00
η^e	0.0811	0.07731	0.0766	0.04167	0.02199	0.01572	0.00996	0
$1-S_0^f$	0.01698	0.012866	0.006967	0.004310	0.002161	0.001236	0.000467	0
$1-S_1^g$	0.000631	0.000485	0.000215	0.000086	0.000041	0.000018	0.000008	0
Φ_0^h	1	0.9967	0.9890	0.9859	0.9847	0.9840	0.9830	0.9830
$(1\sigma_g, 1\sigma_u) (\bar{1}\bar{\sigma}_g, \bar{1}\bar{\sigma}_u)^h$	(-0.0811)	-0.0803	-0.1044	-0.0994	-0.0950	-0.0911	-0.0920	-0.0907
$(1\sigma_g, 1\sigma_u) (\bar{1}\bar{\sigma}_g, \bar{2}\bar{\sigma}_u)^h$	(-0.0662)	(-0.0773)	-0.0740	-0.0794	-0.0769	-0.0753	-0.0775	-0.0765
$(1\sigma_g, 2\sigma_u) (\bar{1}\bar{\sigma}_g, \bar{2}\bar{\sigma}_u)^h$	(-0.0687)	(-0.0650)	(-0.0766)	-0.0739	-0.0707	-0.0735	-0.0733	-0.0719
$(1\sigma_g, 2\pi_u) (\bar{1}\bar{\sigma}_g, \bar{2}\bar{\pi}_u)^h$	(-0.0455)	(-0.0447)	(-0.0428)	(-0.0416)	-0.0398	-0.0393	-0.0400	-0.0388
$(1\sigma_g, 2\sigma_g) (\bar{1}\bar{\sigma}_g, \bar{2}\bar{\sigma}_g)^h$	(-0.0394)	(-0.0376)	(-0.0390)	(-0.0370)	-0.0346	-0.0360	-0.0341	-0.0346
$(1\sigma_g, 3\sigma_g) (\bar{1}\bar{\sigma}_g, \bar{3}\bar{\sigma}_g)^h$	(-0.0290)	(-0.0273)	(-0.0240)	(-0.0226)	(-0.0219)	-0.0224	-0.0230	-0.0225

^a Number of determinants included in Ψ_0 .

^b Energy of Ψ_0 with respect to the SCF energy.

^c Second-order corrected energy: $E_T = E_D + \epsilon^2$.

^d Percent of the correlation energy obtained at this step.

^e η absolute value of the largest coefficient in Ψ^1 .

^f S_0 is the scalar product of Ψ_0 with Ψ_{ex} , the exact eigenvector in the basis.

^g S_1 is the scalar product of the normalized first-order corrected wavefunction $(\Psi_0 + \Psi_1 | \Psi_{ex})$.

^h Coefficients of the most important determinants in Ψ_0 and in Ψ_1 (in parentheses). The determinants are represented by hole-particle pair products.

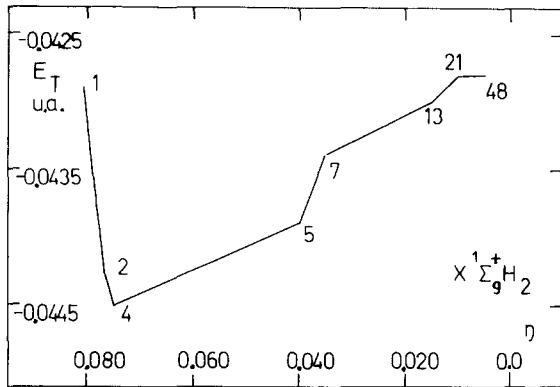


FIG. 3. Evolution of the second-order corrected energies of the 1S ground state, lowest D triplet state, and lowest 1S singlet excited state of Ne atoms as a function of η . Same comments as for Fig. 1.

responding second-order energy correction for the wavefunction Φ_0 is

$$\epsilon_0^2 = \langle \phi_i \phi_j | 1/r_{12} | \phi_k \phi_l \rangle^2 / (\epsilon_k + \epsilon_l - \epsilon_i - \epsilon_j) = a^2 / \Delta E. \quad (29)$$

When D^+ acts on a configuration I belonging to S , it leads to a configuration $|J\rangle = D^+ |I\rangle$, which does not belong to S . Otherwise D^+ acting on $|J\rangle$ would give zero,

$$D^+ |J\rangle = D^+ D^+ |I\rangle = 0. \quad (30)$$

Therefore one may consider the second-order energy correction corresponding to ψ_m . This correction involves the following contribution:

$$\begin{aligned} \epsilon_m^2 &= \sum_I C_{mI}^2 \langle I | H | D^+ I \rangle^2 / (\epsilon_m' - E_I), \\ \epsilon_m^2 &= \sum_I C_{mI}^2 a^2 / [\epsilon_m' - (E_I - \Delta E)], \end{aligned} \quad (31)$$

since $E_J = E_I - \Delta E$, due to the mono-electronic character of H_0 outside of S . ($\epsilon_m' - E_I$) should be small compared to ΔE , since ϵ_m' lies among the E_I . Then, performing a limited development, one obtains

$$\begin{aligned} \epsilon_m^2 &= (a^2 / \Delta E) \left(\sum_I C_{mI}^2 \{ 1 + [(\epsilon_m' - E_I) / \Delta E]^{-1} \} \right), \\ \epsilon_m^2 &\simeq (a^2 / \Delta E) \{ 1 - [(\epsilon_m' - \sum_I C_{mI}^2 E_I) / \Delta E] \} + O(4), \end{aligned} \quad (32)$$

where $O(4)$ represents a fourth-order contribution. The definition of ϵ_m' leads to

$$\epsilon_m^2 = (a^2 / \Delta E) + O(4) = \epsilon_0^2 + O(4). \quad (33)$$

In other words the processes which are possible on all the determinants appearing in two states ψ_i and ψ_j lead to equal contributions and cancel in the transition energy calculation. The absurd n dependency of the transition energy that we had noticed in our model for the Epstein-Nesbet definition of H_0 no longer occurs. This result also holds for higher-order processes in V , and this generalizes the cancellation

of common diagrams previously noticed for the transition energies between nondegenerated determinants.²¹ However, this cancellation is not rigorous in general since it is based on a limited expansion. It would occur exactly if the determinants of the subspace S were degenerate, for instance in an excitonic treatment of a regular system using localized mono-electronic wavefunctions.

In practice we have followed a third procedure, intermediate between the Epstein-Nesbet and Moller-Plesset definition of H_0 for the multiconfigurational case. For the vectorial space T , H_0 is defined by the Epstein-Nesbet partition. The eigenvalues of H_0 associated with the vectors ψ_m are taken as the barycentric values relative to the single determinant energies in the Epstein-Nesbet definition $\epsilon_m'' = \sum_I C_{mI}^2 H_{II}$, ($H_{II} = \langle \Phi_I | H | \Phi_I \rangle$). This definition introduces in the second-order corrections the large terms of the third-order corrections which imply the J_{ij} Coulomb integrals



in the ladder diagrams. The cancellation of the common diagrams in the transition energy does not occur as rigorously but it still happens approximately. If ψ_m is a combination of say two singly excited, $S_z = 1$, determinants, then $\epsilon_m'' \simeq -\epsilon_i + \epsilon_j + J_{ij}$. If $E_0 = \langle \Phi_0 | H | \Phi_0 \rangle$ is taken as the standard zero of energies, the triplet excited determinants obtained by a double excitation $a^+_{m_1} a^+_{n_1} a^+_{p_1} a^+_{n_1}$ on ψ_m have eigenvalues given by the general formula,

$$\begin{aligned} E_I &= \langle \Phi_I | H | \Phi_I \rangle \\ &= \sum_c \epsilon_c (-1)^{n_c} + \sum_c \sum_d (J_{cd} - K_{cd}) (-1)^{n_c + n_d}, \end{aligned} \quad (34)$$

where c and d are holes ($n_c = 1$) or particles ($n_c = 0$) characterizing the state Φ_I and n their occupation number,²⁵

$$\epsilon_m'' - E_I = (\epsilon_m' - E_i') + \sum (J - K) - \sum (J' - K'), \quad (35)$$

where $\sum (J - K)$ and $\sum (J' - K')$ represent two summations over the same number of Coulombic and exchange integrals. These two summations approximately cancel, and the cancellation of common diagrams in the transition energy is still satisfied. As an example one may see that in our model problem [$(n+2)$ H_2 molecules far apart], the cancellation of the diexcitations' effects on Φ_0 and ψ_1 still occurs rigorously.

In a qualitative way, one may say that the absurd n dependency of the transition energy in the generalized Epstein-Nesbet definition of H^0 comes from the following disymmetry.

TABLE II. Convergence of the iterative perturbational process for the E, F singlet ${}^1\Sigma_g^+$ state of H_2 (all energies in atomic units).

ncf	2	3	6	15	48
E_D^a	0.52219	0.50050	0.48905	0.45404	0.47909
E_T^a	0.48287	0.48045	0.47893	0.47888	0.47909
% of E_{corr}^a	91.22	96.84	100.37	100.48	100.00
η^a	0.17865	0.08121	0.02106	0.01683	0
$1-S_0^a$	0.0316	0.0133	0.0078	0.0013	0
$1-S_1^a$	0.0033	0.0028	0.00019	0.00007	0
S_{01}^b	0.0219	0.0388	0.0089	0.0015	0
$(1\sigma_g, 2\sigma_g)^a$	0.7070	0.6950	0.6889	0.6886	0.6847
$(1\sigma_g, 2\sigma_g)(\bar{1}\bar{\sigma}_g, \bar{2}\bar{\sigma}_g)^a$	(0.1786)	0.1820	0.1790	0.1890	0.1892
$(1\sigma_g, 2\sigma_u)(\bar{1}\bar{\sigma}_g, \bar{2}\bar{\sigma}_u)^a$	(-0.0730)	(-0.0812)	-0.0956	-0.0989	-0.0968
$(1\sigma_g, 1\sigma_u)(\bar{1}\bar{\sigma}_g, \bar{2}\bar{\sigma}_u)^a$	(-0.0626)	(-0.0593)	-0.0676	-0.0637	-0.0686
$(1\sigma_g, 2\sigma_u)(\bar{1}\bar{\sigma}_g, \bar{3}\bar{\sigma}_u)^a$	(0.0162)	(0.0173)	(0.0211)	0.0208	0.0208
Φ_0^a	(0.0)	(0.0163)	(-0.0206)	-0.0193	-0.0294
$(1\sigma_g, 1\pi_u)(\bar{1}\bar{\sigma}_g, \bar{1}\bar{\pi}_u)^a$	(0.0276)	(0.0191)	(0.0191)	0.0182	0.0239

^a See corresponding footnotes a-h in Table I.

^b Scalar product of the normalized perturbed wavefunction $\Psi_0 + \Psi_1$ with the exact wavefunction of the ground state.

H^0 involves the nondiagonal Hamiltonian matrix elements between the determinants of the subspace S , while the corresponding interaction of the highly excited states Φ_I outside of S are not included. To restore the cancellation of common diagrams in transition energies, we have built a zeroth-order Hamiltonian H_0' which does not imply the matrix elements between the determinants of the subspace S .

The choice of H_0 recently proposed by Adams²⁶ is still worse. The eigenvalues of H_0 are the eigenvalues of $P_s H P_s$ in S and the sum of the mono-electronic energies outside of S . In the case where S is the ground state single determinant, the energy denominators relative to a diexcitation

$$\begin{pmatrix} j^* & l^* \\ i & k \end{pmatrix}$$

are

$$E_0' - E_I = \epsilon_i + \epsilon_k - \epsilon_j - \epsilon_l - C = E_0 - C - E_I,$$

where C is the sum of electronic repulsions in the ground state. This number increases at least as N (the number of particles of the systems) and ϵ^2 (the second-order energy correction) tend towards a constant instead of increasing as N . One obtains the meaningless corrections of the Brillouin-Wigner series noticed a long time ago by Brueckner.² In the case where S implies several determinants, ϵ_1 is still larger and the second-order correction still lower.

On the contrary the definition proposed by Silverstone²⁷ for E_0 in the case of full degeneracy is identical with our definition in this peculiar case. Since we only calculated the second-order correction energy, the definition of H_0 for the other eigenfunctions of the subspace S has not been studied carefully, but

the definition of H_0 suggested by Silverstone might be useful for the nearly degenerate case.

II. DESCRIPTION OF THE METHOD

A. Definition of a Practical Iterative Procedure for the Construction of ψ_m^0

The multiconfigurational zeroth-order wavefunction ψ_m^0 for the state m may be determined by an iterative procedure selecting the most important determinants to include in ψ_m^0 . One starts from the single determinant, or the evident linear combination of degenerate determinants which is supposed to represent the usual single particle approximation for ψ_m^0 . Let us call $\psi_m^{0(0)}$ this wavefunction, the upper index in parentheses indicating the step of the iterative process; for a closed-shell ground state problem, it will be, for instance, the SCF determinant. This wavefunction is perturbed to the first order, and the most important components in first-order correction to the wavefunction $\psi_m^{1(0)}$ are selected for this state m at this first stage. These configurations are added to those of $\psi_m^{0(0)}$ and one gets thus a subspace $S_m^{(1)}$ of dimension $ncf_m^{(1)}$. The diagonalization of H restricted to the subspace $S_m^{(1)}$ gives a new zeroth-order approximation $\psi_m^{0(1)}$ to the wavefunction of the state m . This function is again perturbed to the first-order by the determinants outside of $S_m^{(1)}$, giving a new first-order wavefunction $\psi_m^{1(1)}$: again, the selection of the most important coefficients in $\psi_m^{1(1)}$ allows an extension of $S_m^{(1)}$ to $S_m^{(2)}$ which has a larger dimension $ncf_m^{(2)}$. The process is iterated until one reaches a stable result and/or the practical/financial limits of the computer. In practice the computer program is built according to the diagrammatic and second quantiza-

TABLE III. Convergence of the iterative perturbational process for the ground state of Ne (all energies in atomic units).

ncf^a	1	4	10	22	41	115
E_D^a	0.0	-0.017572	-0.035693	-0.060082	-0.083039	-0.098953
E_T^a	-0.211791	-0.204340	-0.198096	-0.194204	-0.187715	-0.183120
η^a	0.04474	0.03351	0.02526	0.02094	0.01258	0.00445
Φ_0^a	1	0.997046	0.994571	0.992702	0.990807	0.989539
$(2p_x, 3p_x) (\bar{2}p_x, \bar{3}p_x)^a$	(-0.04474)	-0.04434	-0.04052	-0.03752	-0.03973	-0.03656
$(2p_x, 3p_x) (\bar{2}p_y, \bar{3}p_y)^a$	(-0.03587)	(-0.03351)	-0.03130	-0.02778	-0.02778	-0.02610
$(2s, 3s) (\bar{2}p_x, \bar{3}p_x)^a$	(-0.02555)	(-0.02543)	(-0.02526)	-0.02295	-0.02324	-0.02073
$(2p_x, 3p_x) (2p_y, 3p_y)^a$	(-0.03151)	(-0.02836)	(-0.02345)	-0.02040	-0.02011	-0.01952
$(2p_x, 3p_x)^a$	0.	(0.000573)	(0.01181)	(0.01723)	0.01086	0.00881
$(2s, 3s) (\bar{2}s, \bar{3}s)^a$	(-0.02124)	(-0.02123)	(-0.02123)	(-0.02094)	-0.01939	-0.01773
$(2p_x, 4p_x) (\bar{2}p_x, \bar{4}p_x)^a$	(-0.01515)	(-0.01479)	(-0.01480)	(-0.01481)	-0.01442	-0.01320
$(2p_x, 3p_x) (\bar{2}p_x, \bar{4}p_x)^a$	(-0.01405)	(-0.01540)	(-0.01462)	(-0.01403)	-0.01363	-0.01209
$(2p_x, 3s) (\bar{2}p_x, \bar{3}s)^a$	(-0.01372)	(-0.01291)	(-0.01299)	(-0.01421)	-0.01207	-0.01296

^a See corresponding footnotes a-h in Table I.

tion formalism, the excited configuration being defined by their holes and particles with respect to the self-consistent ground state Φ_0 . When the states Φ_I belonging to S are defined, the states Φ_J outside of S which interact with ψ^0 are generated in a systematic way, by the action of all products $a_i^+ a_j^+ a_k a_l$ and $a_i^+ a_j$ on the determinants Φ_I belonging to S . Then one establishes the matrix elements between Φ_J and ψ^0 ,

$$\langle \Phi_J | H | \psi^0 \rangle = \sum_{k \in S} c_k \langle \Phi_J | H | \Phi_k \rangle \quad (36)$$

by calculating all the matrix elements $\langle \Phi_J | H | \Phi_K \rangle$ in a hole-particle formalism.

The same determinants Φ_J outside of S may be generated several times from different determinants belonging to S , for instance from Φ_K and Φ_L . We avoid the accumulation of identical contributions in the second-order energy correction by the following process. When one builds a determinant Φ_J from a determinant Φ_L , one rejects the corresponding correction if Φ_J interacts with at least one of the previously considered determinants Φ_K , $K < L$, of S . This test is not time consuming since the matrix elements $\langle \Phi_J | H | \Phi_K \rangle$ have to be calculated.

This procedure should allow a rational and progressive construction of the zeroth-order wavefunction ψ^0 for any state m , which becomes better and better when the dimension of S_m increases. Therefore the method will be called hereafter CIPSI (configuration interaction by perturbation with multiconfigurational zeroth-order wavefunction selected by iterative process). The adequacy of $\psi_m^{0(n)}$ and $S_m^{(n)}$ in the per-

turbation at the stage n of the iterative procedure may be tested by considering the values $\eta_m^{(n)}$ of the largest coefficient in $\Psi_m^{1(n)}$. Hereafter $\eta_m^{(n)}$ will be called the criterion of adequacy of the zeroth-order wavefunction to the perturbation at the stage n . This procedure is superior to a selection which keeps all the determinants which are closest in energy to the zeroth-order determinant. One often includes in the CI calculation of a ground state the singly and low-lying doubly excited states, but singly excited determinants do not interact with the SCF ground state Φ_0 (Brillouin's theorem) and the low-lying doubly excited may have smaller interactions with Φ_0 and therefore smaller coefficients in the perturbed wavefunction than high-energy doubly excited determinants.

The eigenvalue $\mathcal{E}_m^{(n)}$ associated with $\psi_m^{0(n)}$ after the diagonalization of H restricted to $S_m^{(n)}$ is equal to the first-order corrected energy, according to our definition of the perturbation expansion in the preceding section,

$$\mathcal{E}_m^{(n)} = E_m^{0(n)} + \epsilon_m^{1(n)}, \quad (37)$$

$E_m^{0(n)}$ being the barycentric energy associated with $\psi_m^{0(n)}$. When $ncf_m^{(n)}$ increases with n , the energy $E_m^{(n)}$ should tend towards the exact eigenvalue of H . For instance in the ground state problem we get an increasing part of the correlation energy. On the contrary the second-order perturbation energy correction $\epsilon_m^{2(n)}$ arising from determinants interacting more weakly with ψ_m^0 will decrease towards zero when $ncf_m^{(n)}$ tends towards the total number of determinants.

The energy of the calculated level is then calculated as

$$E_m^{(n)} = \epsilon_m^{1(n)} + \epsilon_m^{2(n)} = \epsilon_m^{0(n)} + \epsilon_m^{1(n)} + \epsilon_m^{2(n)}. \quad (38)$$

Of course, in practice, except for very small problems in limited basis set, the largest part of the correlation energy remains obtained from ϵ^2 , S representing only a small part of the total vectorial space.

It is interesting here to note the three main differences between our method and the method previously suggested by Gershgorin and Shavitt,²⁴ who perturb the ground state wavefunction ψ^0 resulting from the diagonalization of the CI matrix restricted to the ground state and the k lowest (doubly) excited determinants.

Our method allows a less arbitrary construction of ψ_m^0 since the most important components of ψ_m are progressively introduced. Thus a small number of determinants in S should be sufficient to reach the same degree of accuracy.

Our method is more general and allows the treatment of excited states as well as of the ground state.

The Gershgorin and Shavitt procedure is based on a generalized Epstein-Nesbet partition of the Hamiltonian and therefore should lead to the absurd consequences of the noncancellation of common diagrams in transition energies, while our definition of the un-

perturbed Hamiltonian avoids these difficulties, even on large systems.

B. Comparison of the Proposed Procedure with the Usual Perturbation Expansion from a Single Determinant ψ_0

Our process is limited to the second-order in energy, and it is hoped that it should give reliable results in cases where the usual perturbation expansion from a single determinant wavefunction ψ_0 would certainly diverge or give meaningless first-order corrections. Nevertheless, it may be interesting from a theoretical point of view to interpret our second-order result after the diagonalization of a rather large CI, in terms of second-, third-, fourth-order contributions of the usual RS perturbation expansion from a single determinant ψ_0 . Let us suppose, for instance, that we are interested in a nondegenerate SCF ground state Φ_0 .

In the classical Rayleigh-Schrödinger procedure, assuming a choice of H^0 which ensures $\epsilon_0^1=0$, the second-order correction,

$$\epsilon^2 = \sum_I [\langle \Phi_0 | H | \Phi_I \rangle^2 / (E_0 - E_I)], \quad (39)$$

implies the interaction between Φ_0 and all the doubly excited determinants Φ_I . The third-order correction,

$$\epsilon_0^3 = \sum_I \sum_J \frac{\langle \Phi_0 | V | \Phi_I \rangle \langle \Phi_I | V | \Phi_J \rangle \langle \Phi_J | V | \Phi_0 \rangle}{(E_0 - E_I)(E_0 - E_J)}, \quad (40)$$

represents the interaction between the doubly excited determinants of ψ_0^1 while

$$\epsilon_0^4 = -\epsilon_0^2 \langle \psi_0^1 | \psi_0^1 \rangle + \sum_I \sum_J \sum_K \frac{\langle \Phi_0 | V | \Phi_I \rangle \langle \Phi_I | V | \Phi_J \rangle \langle \Phi_J | V | \Phi_K \rangle \langle \Phi_K | V | \Phi_0 \rangle}{(E_0 - E_I)(E_0 - E_J)(E_0 - E_K)} \quad (41)$$

involves interactions of the diexcited configurations with the singly, doubly, triply, and quadruply excited configurations.

Let us suppose that S has included the most important $S_0^{(1)}$ doubly excited determinants in ψ_0^1 . The diagonalization of H restricted to $S_0^{(1)}$ implies a part of the second-order, third-order, etc., corrections, characteristic of the interaction between the ground state and the most important doubly excited determinants. The new zeroth-order wavefunction $\psi_0^{0(1)}$ takes approximately the form

$$\psi_0^{0(1)} \simeq \Phi_0 + \sum_{I \in S_0^{(1)}} [\langle \Phi_0 | V | \Phi_I \rangle \Phi_I / (E_0 - E_I)], \quad (42)$$

where the summation over I is restricted to the doubly excited configurations belonging to S . Then the second-order correction in our procedure

$$\begin{aligned} \epsilon_0^{2(1)} = & \sum_{J \in S_0^{(1)}} \frac{\langle \psi_0^{0(1)} | V | \Phi_J \rangle^2}{(E_0^{(1)} - E_J)} \simeq \sum_J \frac{\langle \Phi_0 | V | \Phi_J \rangle^2}{(E_0^{(1)} - E_J)} \\ & + \sum_{I \in S} \sum_{J \in S} 2 \frac{\langle \Phi_0 | V | \Phi_I \rangle \langle \Phi_I | V | \Phi_J \rangle \langle \Phi_J | V | \Phi_0 \rangle}{(E_0^{(1)} - E_I)(E_0^{(1)} - E_J)} \\ & + \sum_{I \in S} \sum_{J \in S} \sum_{K \in S} \frac{\langle \Phi_0 | V | \Phi_I \rangle \langle \Phi_I | V | \Phi_J \rangle \langle \Phi_J | V | \Phi_K \rangle \langle \Phi_K | V | \Phi_0 \rangle}{(E_0^{(1)} - E_I)(E_0^{(1)} - E_J)(E_0^{(1)} - E_K)}. \quad (43) \end{aligned}$$

TABLE IV. Convergence of the iterative perturbational process for the lowest 1S singlet excited state of Ne (all energies in atomic units).

ncf^a	6	11	17	18
E_D^a	1.83972	1.75679	1.71793	1.72148
E_T^a	1.37327	1.43889	1.47419	1.47220
η^a	-0.08718	-0.06268	-0.05459	-0.02957
$(2p_x, 3p_x)^a$	0.408248	0.396088	0.393043	0.395581
$(2p_x, 3p_x)(\bar{2}p_x, \bar{3}p_x)^a$	(-0.08718)	-0.11419	-0.091398	-0.08771
$(2s, 3s)^a$	(-0.08705)	-0.09890	-0.095836	-0.09615
$(2p_x, 3p_x)(\bar{2}p_y, \bar{3}p_y)^a$	(-0.07260)	(-0.06268)	-0.07032	-0.06757
Φ_0^a	(0.0)	(0.0)	(-0.05459)	-0.04452
$(2p_x, 3p_x)(\bar{2}p_y, \bar{3}p_y)^a$	(-0.06573)	(-0.05141)	(-0.04123)	(-0.02957)
$(2p_x, 4p_x)^a$	(-0.02806)	(-0.02934)	(-0.02902)	(-0.02875)

^a See corresponding footnotes a-h in Table I.

The first summation of Eq. (43) gives the part of the classical ϵ_0^2 which was not already given by the diagonalization of H restricted to S . The second term is a part of the classical $S_0^{(1)}$ third-order correction, representing the interaction between the important (Φ_L) and less important (Φ_J) doubly excited configuration. The only lacking third-order terms represent the interaction between the doubly excited determinants which have weak coefficients in ψ_0^1 . The process therefore selects the large third-order terms of the classical expansion.

The third term in Eq. (43) gives fourth-order corrections in the classical expansion, representing the interaction of the most important doubly excited configurations with singly, doubly, triply, and quadruply excited determinants. One may notice that this contribution includes some fourth-order unlinked terms.² These unlinked contributions cancel the effect of the normalization of ψ_0 . ϵ_0 , the energy of the multiconfigurational ψ^0 wavefunction, actually involves the terms $-\epsilon^2 \langle \psi^1 | \psi^1 \rangle$ which cancel with unlinked terms in the triple summation of Eq. (43). As will be seen in the numerical applications, some singly or triply excited determinants appear in diagonalized subspace S , when the process is iterated far enough. These determinants would not appear in ψ_0^1 in the classical expansion, but in ψ_0^2 . In such a case ϵ_0^1 includes some fourth-order energy corrections and ψ_0^1 implies up to 5 times excited determinants.

The first-order wavefunction ψ^1 obtained from the multiconfigurational ψ_0 contains some quadriexcited configurations, which are obtained from the most important diexcited configurations. Then the most important quadriexcited configurations necessarily appear in ψ^1 with a correct coefficient since the quadriexcited determinants coefficients in the classical second-order wavefunction are the products of the diexcited determinant coefficient in the classical first-order wavefunction ψ^1 .²⁸

C. Representation of the Excited States

No specific problem occurs for the calculation of the excited states which are the lowest states of their

symmetry. If the excited state is not the lowest of its symmetry, one must consider the problem of its orthogonality with the ground state. Two procedures may be suggested.

One may calculate independently the excited state by the same procedure as the ground state, totally ignoring the orthogonality problem between ψ_m^0 for the excited state at a given level of accuracy and the corresponding ψ_0^0 wavefunction for the ground state. Anyway, the procedure should tend towards the exact wavefunctions and energies and there is no risk of falling down on the lower state. The scalar product between the ψ^0 wavefunctions for the two states, $\langle \psi_m^0 | \psi_0^0 \rangle$, may be calculated then and gives an idea about the accuracy of the wavefunction.

One may, on the contrary, work simultaneously on two (or more) states of the same symmetry ψ_m and ψ_n selecting S as the union of the two subspaces S_m and S_n relative to the two states and the same degree of accuracy η on the perturbed coefficients. Then the diagonalization of $S = S_m U S_n$ gives orthogonal zeroth-order approximations ψ_m^0 and ψ_n^0 . The first-order perturbed wavefunctions are also orthogonal as demonstrated by Cohen and Dalgarno,²⁹

$$\langle \psi_m^0 + \psi_m^1 | \psi_n^0 + \psi_n^1 \rangle = 0,$$

and these functions may be used in the calculations of transition moment between ψ_m and ψ_n , since for the calculation of this quantity one must use orthogonal wavefunctions.

A less symmetrical procedure would consist of perturbing a wavefunction ψ_m^0 which has been previously orthogonalized by a Schmidt procedure to the already calculated wavefunction ψ_0^0 for the lowest state.

III. NUMERICAL EXAMPLES

Three typical problems have been chosen to test the CIPSI method.

The hydrogen molecule (two electrons) for which the exact solution in the basis, and even the absolute exact solution, are available;

The neon atom (10 electrons);

The MgO molecule (20 electrons) for which important correlation effects seem to appear in the transition energies, since the HF-calculated energies do not allow the interpretation of the experimental spectrum.

Several states have been calculated for each of these systems. The chosen basis set for the H₂ molecule was a 16 Slater-type AO's basis set, built from the basis of Weiss, McLean, and Yoshimine³⁰ and 2*pπ* AO's with a 0.45 Slater exponent. The calculation was made for a 2 a.u. internuclear distance.

For the neon atom, we used the double-zeta basis set obtained by Bagus,³¹ from a minimization of the SCF ground state energy; it is not studied to obtain good correlation and transition energies, but we have not improved it, since our purpose, mainly methodological, was to study the way to approach the exact solution in a given basis set.

For the MgO molecule, the basis is a double-zeta basis set proposed by Clementi³² for the Mg and O atoms. The internuclear distance is 3.3 a.u.

Tables I and II report the results for the $X^1\Sigma^+$ and $E, F^1\Sigma^+$ states of H₂; Fig. 1 also includes the energy concerning the $b^3\Sigma_u$ state. The $E, F^1\Sigma^+$ state has been chosen because, being of the same symmetry as the ground state, its attainment may present special difficulties, in our method, and because it is known as requiring a multiconfigurational representation.

In Tables III and IV, the results are reported for the 1S_0 and the first singlet state of the same symmetry; Fig. 2 also includes the energy results for the lowest 3D_0 state.

In these tables and figures, η represents the "criterion of adequacy of Ψ^0 ," i.e., the largest coefficient in Ψ^1 (in absolute value). Figures 3 and 4 give the detailed evolution of the ground state energies for H₂ and Ne when η decreases. The results for the four lowest states of MgO (i.e., $X^1\Sigma^+$, $^3\Pi$, $A^1\Pi$, and $^3\Sigma$) are reported in Fig. 5. A more detailed discussion of the transition energies of MgO is given elsewhere.³³

For the H₂ ground state, the classical second-order energy correction (with the Epstein-Nesbet denomi-

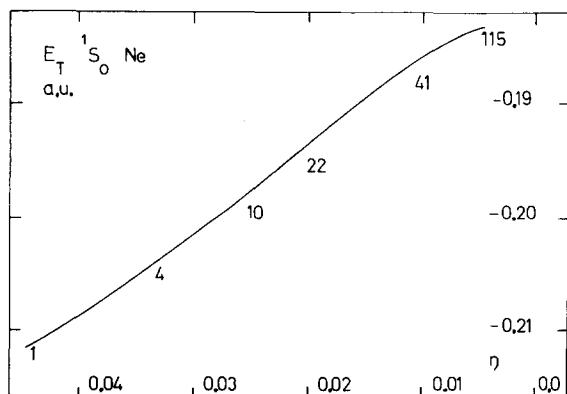


FIG. 4. Detailed evolution of the second-order corrected energies of the ground state of Ne atom as a function of η .

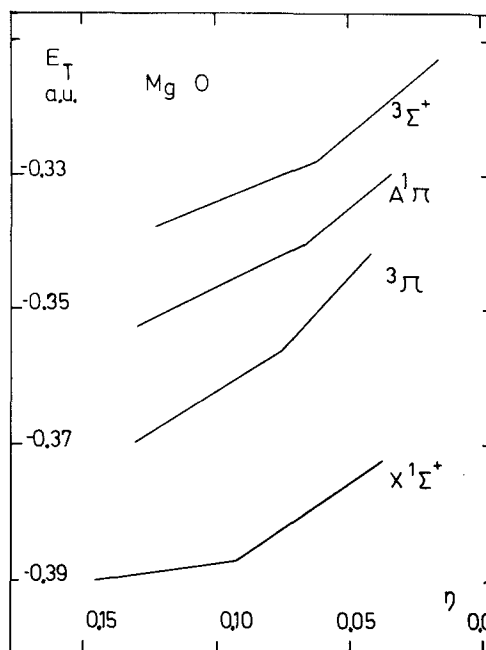


FIG. 5. Evolution of the four lowest states of MgO as a function of η . The "SCF" energies, which could not be represented in this figure, were, respectively, 0.0 for $X^1\Sigma^+$, 0.01328 for $^3\Pi$, 0.04384 for $A^1\Pi$, and -0.02496 for $^3\Sigma^+$.

nators) from the single determinant Ψ^0 gives 100.2% of the correlation energy in the basis. This result compares very well with the analogous result obtained by Schulmann and Kaufman⁹ in a larger basis set of Gaussian orbitals. However in that case, the agreement with the exact solution may be somewhat fortuitous, since the zeroth-order wavefunction with four determinants gives after perturbation 104% of the correlation energy in the basis. This fact demonstrates that cancellations occur between large third-order terms. However, it appears that in that case at least it is better to perturb a wavefunction ψ^0 including only a few determinants than to perform a CI with the most important excited configurations (compare in Table I the results E_T for $ncf=2$, with the results E_D for $ncf=21$).

The ground state energy of the Ne atom behaves differently, the energy growing up when η decreases. This is due to the progressive inclusion of large third-order terms in the perturbed energy. Let us consider for instance Φ_0 and the two sets of most important determinants, namely

$$\Phi_1 = \begin{pmatrix} 3p_x & 3\bar{p}_x \\ 2p_x & 2\bar{p}_x \end{pmatrix} \quad (\text{and equivalents})$$

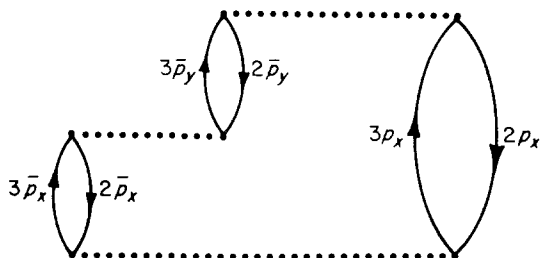
and

$$\Phi_2 = \begin{pmatrix} 3p_x & 3\bar{p}_y \\ 2p_x & 2\bar{p}_y \end{pmatrix} \quad (\text{and equivalents}).$$

The third order includes the interactions

$$\langle \Phi_0 | V | \Phi_1 \rangle \langle \Phi_1 | V | \Phi_2 \rangle \langle \Phi_2 | V | \Phi_0 \rangle / \Delta E_1 \Delta E_2$$

visualized by the ring diagram



Then

$$\langle \Phi_0 | V | \Phi_1 \rangle = (2p_x 3p_x, 2p_x 3p_x) = a,$$

$$\langle \Phi_0 | V | \Phi_1 \rangle = \langle \Phi_1 | V | \Phi_2 \rangle = (2p_x 3p_x, 2p_y 3p_y) = b,$$

and the corresponding third-order correction is equal to $ab^2/\Delta E_1 \Delta E_2$. Since a is positive, this contribution is positive. Such third-order positive corrections between $(n=2 \rightarrow n=3)^2$ diexcited states are very numerous and are progressively included in our process. Such a phenomenon occurs in N_2 as noticed by Grimaldi³⁶ and in conjugated molecules with double and triple bonds.³⁵ This phenomenon also explains the increase in the curves of MgO (Fig. 5). The variations in the correlation energies are at most of the order of 10%.

As far as we know, these perturbation techniques had not been applied before to excited states. Our results show that the perturbation techniques are able to give reasonable results for excited states. Some interactions occur with singly and doubly excited configurations which lie close in energy to the perturbed determinants, and the perturbation convergence may be slower than for the ground state, the value of η for the first iterations being much larger. But the inclusion of a small number of determinants in Ψ^0 for the excited state gives the same type of accuracy as for the ground state with a single determinant Ψ^0 . One may see from Figs. 1, 2, and 5 that the energies of the different states vary in a parallel way when the η values are comparable, the resulting transition energy being more stable than the energy of each state.

The importance of the inclusion of correlation effects in transition energies appears clearly from the case of the $X^1\Sigma_g^+ \rightarrow B^3\Sigma_u$ transition of H_2 , where the correlation energy is much smaller in the triplet state than in the ground state, and from the case of MgO where the correlated energies give a good agreement with the experimental spectrum while the single determinant spectrum was completely off.^{33,36}

The "generalized Epstein-Nesbet" definition of H_0 (see Sec. I) has been tested for H_2 . It gives a much slower convergence of the process, especially for the excited states.

Concerning the wavefunctions, the overlap of Ψ^0 and $\Psi^0 + \Psi^1$ (normalized) with the exact wavefunction

Ψ_{ex} has been calculated for H_2 . Again it appears more worthwhile to perturb a wavefunction Ψ^0 with only a few determinants than to diagonalize a CI matrix truncated to the most important determinants (see lines 1- S_0 and 1- S_1 of Tables I and II). In the case of Ne with a 41-determinant Ψ^0 wavefunction, 20 000 interacting determinants of the correct symmetry have been included in Ψ^1 . In Mg-O for $ncf=16$, 130 000 determinants were included in Ψ^1 .

We have reported in Tables I-IV, the values of the most important coefficients in Ψ^0 and (or) Ψ^1 , for the various iterations, in order to give an idea about the stability of the components of the wavefunction. The coefficients of the determinants which appear in Ψ^1 from the first iteration are rather stable from one iteration to the other. One may notice that some determinants, which only appear in $\Psi^{2(0)}$ when one builds $\Psi^{0(0)}$ from the minimal number of determinants [smallest $ncf(0)$ value], appear soon to be more important than the other determinants of $\Psi^{1(0)}$ and are included in Ψ^0 after some iterations. For instance the ground state determinant Φ_0 appears rapidly with a correct order of magnitude in the $E, F^1\Sigma_g^+$ state of H_2 . Similarly the singly excited configurations ($2p_x \rightarrow 3p_x$) appear quite rapidly in the ground state wavefunction of the Ne ground state. The ground state wavefunction of MgO also has an important component on the singly excited ($6\sigma \rightarrow 7\sigma$) determinant.³³ The process seems able to give the important components of $\Psi^{2(0)}$.

IV. CONCLUSION

The method presented in Sec. I allows us to perturb a multiconfigurational wavefunction to take into account its interaction with the determinants which are not included in Ψ^0 . We have demonstrated that the usual careless choices of the unperturbed Hamiltonian H_0 may lead to meaningless second-order corrected transition energies between two states Ψ^1 and Ψ^2 , even when the Rayleigh-Schrödinger perturbation expansion converges for both states. A proper definition of H_0 has been proposed, which ensures the cancellation of common diagrams in transition energies. Contrary to the previous analogous treatments, the method is valid for excited states. The practical iterative CIPSI procedure has been proposed in Sec. II to build better and better Ψ^0 zeroth-order wavefunctions, choosing progressively the most important determinants. It has been shown that the method takes into account the main interactions appearing in the usual third- and fourth-order energy corrections of the RS series from a single determinant wavefunction.

In Sec. III of this paper, we have presented some tests of the method. The convergence of this method has been studied on the ground state and several excited states of H_2 for which the exact solutions in the basis were available. Several states of Ne have

also been studied. One obtains a rapid stabilization of the results. But the main aim of this work was to establish a reliable theoretical procedure for the calculation of transition energies on molecules for which the single particle model gives poor results. In particular the method has been applied to the controversial problem of Mg-O, for which the HF-

calculated energies do not allow the interpretation of the experimental spectrum. The method presented here gives correctly the feature of this spectrum.³³ The various examples show the importance of differential correlation effects on transition energies. Further work will be devoted to spectroscopic problems appearing in solar and stellar physics.

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