

Jordan Journal of Physics

ARTICLE

Amending the LCAO Basis Set in the Hartree-Fock-Roothaan Approximation to First-Order Perturbation Theory

B. Anak^a, T. Benlecheb^b, Y. Djebli^a, Y. Belhocine^a and M. Bencharif^a

^a*Faculté des Sciences Exactes, Département de Chimie, Université Mentouri Constantine, Algeria.*

^b*Faculté des Sciences, Département de Chimie, Université A. Laghrour, Khenchela, Algeria.*

Received on: 13/11/2011; Accepted on: 9/5/2012

Abstract: We have formulated the first-order Hartree-Fock equations for multielectron systems exposed to an external perturbation in the LCAO (Linear Combination of Atomic Orbital) approximation. The perturbation theory corrections to these equations have been found in the form of expansions in unperturbed equations and terms which depend explicitly on this perturbation. The ideas leading to this amendment are implicit in previous studies, but the significance of its existence has not yet been sufficiently emphasized and its simple explicit form has not been presented. With the proposed approach, one may obtain the first-order correction perturbation energy in the presence of any perturbation, knowing merely the overlap. This may further facilitate linear scaling computation of the energy correction.

Keywords: Hartree-Fock; LCAO; Perturbation; Energy correction.

Introduction

For multielectronic systems, the calculation used is the algebraic form of Hartree-Fock (HF) method like Hartree-Fock-Roothaan (HFR) [1, 2]. In this formalism, the minimum energy of the system is a function of the orbital coefficients and nonlinear parameters of the basis functions. The physical properties of a system under external field are described with the aid of polarizabilities, susceptibilities and other parameters based on the framework of quantum mechanics expressed in terms of perturbation theory which represents a very complex problem in computational and formalism aspect [3]. The equations of Hartree-Fock perturbation theory lead to the equations of McWeeny formulae with all orders, obtained in terms of the unperturbed Hamiltonian and density matrix. It is also shown that the perturbation may be obtained directly, without separating the orders, and that the approach is related to earlier steepest-descent methods [4]. The coupled-perturbation theory [5]

leads to good accuracy [6–10]. However, there is a dispersion in the values of calculated polarizability [7]. In [6, 11], the optimum basis set of atomic orbitals to calculate polarizabilities can be found by minimization methods of the first and second orders. In the magnetic case of perturbation, all spectral states are needed in Vanvleck formulation which leads to calculation limit and invariant problems [12, 14].

It has been seen that orders are not explicit or separated from all variants of the perturbation method derived from McWeeny formulae [13]. In the present work, we use the London unperturbed base with Gauge factor bypass invariant problem [14] to achieve the separated order perturbation method. It is an original way to formulate the theory of first-order perturbation taking account of the effect of perturbation on the basis set. From the formalism developed by MacWeeny, we show explicitly the action of a perturbation on the different quantities that are

associated with it. The special feature of the writing in our equations lies in the fact to recover the unperturbed state just in quashing the terms relating to the perturbation. To illustrate this, we have attached an annex with the case of a magnetic perturbation in which the basis set is represented by the perturbed GIAO introduced by London [14].

Hartree–Fock–Roothaan equations

The Hartree-Fock-Roothaan [1-3] method is constructed on the MO (Molecular Orbital) theory [4, 5] and the LCAO (Linear Combination of Atomic Orbital) approach, where the OM $\{\Psi_i\}$ are simply expressed in terms of a basis set of atomic orbitals $\{\phi_r\}$ as follows:

$$\Psi_i = \sum_{r=1}^n C_{ir} \cdot \phi_r ; \quad (1)$$

where n represents the dimensional basis used and the set $\{C_{ir}\}$ the OM $\{\Psi_i\}$ coefficients of development.

The pseudo-secular equations of the method are expressed as:

$$FC_i = e_i SC_i ; \quad (2)$$

where F represent the Fock operator and can be expressed by the relation $F = h + G$, in which h and G are respectively the core operator and the bioelectronic repulsion operator; $\{e_i\}$ is a set of the OM energies and S signifies the overlap matrix whose elements are written as follows:

$$S_{ij} = \langle \phi_i^* | \phi_j \rangle . \quad (3)$$

The coefficient vectors of the molecular orbital are pseudo-normalized, so:

$$C_i^+ SC_j = \delta_{ij} . \quad (4)$$

In this notation, the exposing label + means the adjunction operation and δ_{ij} represents the Krönecker symbol.

In general, we note $Z_{ij} = X_i^+ Z X_j$ any scalar product, where X_i and X_j are vector-columns and Z represents a matrix.

For example, in eq. (4), S_{ij} is defined as:

$$S_{ij} = C_i^+ SC_j .$$

Finally, the system to be resolved is expressed as follows:

$$(F - e_i \cdot S) C_i = 0 ; \quad (5.a)$$

$$C_i^+ SC_j = \delta_{ij} . \quad (5.b)$$

The energy orbital e_i is obtained by using eq. (2).

Multiplying at left by C_i^+ yields

$$C_i^+ FC_i = e_i C_i^+ SC_i .$$

Based on the normalization condition, we have:

$$e_i = C_i^+ FC_i ; \quad (6.a)$$

$$e_i = F_{ii} . \quad (6.b)$$

The total electronic energy can be expressed by:

$$E = \sum_{i=1}^M C_i^+ H C_i .$$

With $H = h + F$ and $F = h + G$, we obtain $H = 2h + G$.

M indicates the label of the HOMO (Highest Occupied Molecular Orbital).

We can rewrite:

$$E = \sum_{i=1}^M 2C_i^+ h C_i + \sum_{i=1}^M C_i^+ G C_i .$$

Taking:

$$E_1 = \sum_{i=1}^M 2C_i^+ h C_i \quad (7.a)$$

$$E_2 = \sum_{i=1}^M C_i^+ G C_i , \quad (7.b)$$

we obtain

$$E = E_1 + E_2 . \quad (7)$$

Note that $C_i^+ h C_i$ corresponds to a scalar product which can be developed meaning the property:

$$X_i^+ Z Y_i = \sum_{r=1}^n \sum_{s=1}^n X_{ir} Z_{rs} Y_{is} .$$

So:

$$E = \sum_i^M (2h_{ii} + G_{ii}) . \quad (8)$$

By using LCAO basis $\{\phi_r\}$ and development (1), the expression of E is obtained as follows:

$$E = \sum_{i=1}^M \sum_{r=1}^n \sum_{s=1}^n 2C_{ir}^* h_{rs} C_{is} + \sum_{i=1}^M \sum_{r=1}^n \sum_{s=1}^n C_{ir}^* G_{rs} C_{is}$$

or:

$$E = \sum_{r=1}^n \sum_{s=1}^n h_{rs} \left(\sum_{i=1}^M 2C_{ir}^* C_{is} \right) + \frac{1}{2} \sum_{r=1}^n \sum_{s=1}^n \left(\sum_{i=1}^M 2C_{ir}^* C_{is} \right).$$

Defining the matrix density by:

$$P_{rs} = \sum_{i=1}^M 2C_{ir}^* C_{is}, \quad (9)$$

we can write:

$$E = \sum_{r=1}^n \sum_{s=1}^n P_{rs} \left(h_{rs} + \frac{1}{2} F_{rs} \right), \quad (10)$$

with:

$$\begin{cases} F_{rs} = h_{rs} + G_{rs} \\ G_{rs} = \sum_{t=1}^n \sum_{u=1}^n P_{tu} \cdot g_{rstu} \\ g_{rstu} = \gamma_{rstu} - \frac{1}{2} \gamma_{ruts} \end{cases}$$

The matrix elements F_{rs} , h_{rs} and γ_{rstu} are respectively the Fock integrals, the Hamiltonian core integrals and the bi-electronic repulsion integrals, defined by:

$$\begin{cases} F_{rs} = \langle \phi_r^* (1) | F(1) | \phi_s (1) \rangle \\ h_{rs} = \langle \phi_r^* (1) | h(1) | \phi_s (1) \rangle \\ \gamma_{rstu} = \left\langle \phi_r^* (1) \phi_s (1) \left| \frac{e^2}{r_{12}} \right| \phi_t^* (2) \phi_u (2) \right\rangle. \end{cases}$$

Effects of perturbation

Our theoretical approach is applied to any physical phenomenon where a perturbation modifies the basis set in the framework of HFR method, allowing the calculation of the parameters related to the presence of an external electric or magnetic field.

In principle, all equations stay formally unchanged, but they will be evaluated by passing the new perturbed basis $\{\chi_r\}$.

The introduction of an external field induces a perturbation that affects all sizes (F , C , e_i , E , H , S) and can develop into a series of perturbation in the following way:

$$\begin{bmatrix} F = \sum_{p \geq 0} F^p & C_i = \sum_{p \geq 0} C_i^p & e_i = \sum_{p \geq 0} e_i^p \\ E = \sum_{p \geq 0} E^p & H = \sum_{p \geq 0} H^p & S = \sum_{p \geq 0} S^p \end{bmatrix}.$$

The exposing notation signifies the different orders of development, where $p = 0, 1, 2, \dots$ represent respectively the unperturbed state, the first perturbation order, the second perturbation order, and so on.

The decomposition in perturbation series of relations (5.a) and (5.b) gives:

$$\sum_{p \geq 0} \sum_{q \geq 0} F^p C_i^q - \sum_{p \geq 0} \sum_{q \geq 0} \sum_{t \geq 0} e_i^p S^q C_i^t = 0; \quad (11.a)$$

$$\sum_{p \geq 0} \sum_{q \geq 0} \sum_{t \geq 0} C_i^p S^q C_j^t = \delta_{ij}. \quad (11.b)$$

Orders' separation

For the physical meaning, the sizes in the equation must be in the same order, and hence an order separation is required. The calculation technique of the separation process is summarized as follows:

We call $m = p + q$ the perturbation order with $m \geq 0$; then $q = m - p$ where $q \geq 0$, so $m - p \geq 0$ and $p \leq m$; since $p \geq 0$, finally $0 \leq p \leq m$. Then, we simply replace the couple of variables (p, q) by (p, m) . So, the double summation can be expressed by:

$$\sum_{p \geq 0} \sum_{q \geq 0} F^p C_i^q = \sum_{m \geq 0} \sum_{p=0}^m F^p C_i^{m-p}.$$

In the same manner $m = p + q + t$; then $t = m - (p + q)$ with $t \geq 0$, so $m - (p + q) \geq 0$ or $q \leq m - p$; since $q \geq 0$, finally $0 \leq q \leq m - p$. As before, we replace the variables (p, q, t) by (p, q, m) . So, the triple summation is expressed as:

$$\sum_{p \geq 0} \sum_{q \geq 0} \sum_{t \geq 0} e_i^p S^q C_i^t = \sum_{m \geq 0} \sum_{p=0}^m \sum_{q=0}^{m-p} e_i^p S^q C_i^{m-(p+q)}.$$

The pseudo-secular eqs. (11.a) are written as:

$$\sum_{m \geq 0} \left\{ \sum_{p=0}^m F^p C_i^{m-p} - \sum_{p=0}^m \sum_{q=0}^{m-p} e_i^p S^q C_i^{m-(p+q)} \right\} = 0 \quad (12.a)$$

So, it is clear that the perturbed HF equation in the order m is given by:

$$\sum_{p=0}^m F^p C_i^{m-p} - \sum_{p=0}^m \sum_{q=0}^{m-p} e_i^p S^q C_i^{m-(p+q)} = 0. \quad (12.b)$$

The same way applied to pseudo-orthonormality condition (11.b) leads to:

$$\sum_{m \geq 0} \sum_{p=0}^m \sum_{q=0}^{m-p} C_i^{+p} S^q C_j^{m-(p+q)} = \delta_{ij}. \quad (13.a)$$

By extracting the term of zero order ($m = 0$), we can write:

$$C_i^{+0} S^0 C_j^0 + \sum_{m \geq 1} \sum_{p=0}^m \sum_{q=0}^{m-p} C_i^{+p} S^q C_j^{m-(p+q)} = \delta_{ij}.$$

Based on the orthonormality condition (eq.4), we obtain:

$$\sum_{m \geq 1} \sum_{p=0}^m \sum_{q=0}^{m-p} C_i^{+p} S^q C_j^{m-(p+q)} = 0.$$

Separating the orders, we have:

$$\sum_{p=0}^m \sum_{q=0}^{m-p} C_i^{+p} S^q C_j^{m-(p+q)} = 0. \quad (13.b)$$

Note that in the case of zero order ($m = 0$), we find the solutions corresponding to the absence of any perturbation:

$$F^0 C_i^0 = e_i^0 S^0 C_i^0;$$

$$C_i^{+0} S^0 C_j^0 = \delta_{ij}.$$

With respect to first-order perturbation ($m = 1$), eqs. (12.b) and (13.b) take the following form:

$$\left. \begin{aligned} F^1 C_i^0 + F^0 C_i^1 - \\ (e_i^1 S^0 C_i^0 + e_i^0 S^1 C_i^0 + e_i^0 S^0 C_i^1) = 0 \end{aligned} \right\}; \quad (14.a)$$

$$C_i^{+1} S^0 C_j^0 + C_i^{+0} S^1 C_j^0 + C_i^{+0} S^0 C_j^1 = 0. \quad (14.b)$$

First-order correction to energy orbital e_i^I

Multiplying the left expression of eq. (14.a) by C_i^{+0} gives the form:

$$\left. \begin{aligned} C_i^{+0} F^1 C_i^0 + C_i^{+0} F^0 C_i^1 - \\ (e_i^1 C_i^{+0} S^0 C_i^0 + e_i^0 C_i^{+0} S^1 C_i^0 + e_i^0 C_i^{+0} S^0 C_i^1) \end{aligned} \right\} = 0.$$

Taking into account the conditions $C_i^{+0} S^0 C_i^0 = 1$, $C_i^{+0} F^0 = e_i^0 C_i^{+0} S^0$ and with $C_i^{+0} F^1 C_i^0 = F_{ii}^1$; $C_i^{+0} S^1 C_i^0 = S_{ii}^1$, we obtain:

$$\left. \begin{aligned} F_{ii}^1 + e_i^0 C_i^{+0} S^0 C_i^1 - \\ (e_i^1 + e_i^0 S_{ii}^1 + e_i^0 C_i^{+0} S^0 C_i^1) = 0 \end{aligned} \right\},$$

from which, we can write the e_i^I expression

$$\left. \begin{aligned} e_i^1 &= F_{ii}^1 - e_i^0 S_{ii}^1 \\ e_i^1 &= C_i^{+0} F^1 C_i^0 - e_i^0 C_i^{+0} S^1 C_i^0 \end{aligned} \right\}. \quad (15)$$

Principles of calculating S_{ii}^I

In this method, the perturbation changes the basis set; then it is possible to develop S in a series of perturbation with:

$$S = \sum_{p \geq 0} S^p.$$

In addition, we can develop S near a given value of perturbation, following a series of Mac-Laurin. By identifying these two developments, one can express the analytical forms of S^p with $p \geq I$.

Calculation of F_{ii}^I

Its expression is given by:

$$\left. \begin{aligned} F^1 &= h^1 + G^1(P^1) \\ F_{rs}^1 &= h_{rs}^1 + \sum_{t=1}^n \sum_{u=1}^n (P_{tu}^1 g_{rstu}^0 + P_{tu}^0 g_{rstu}^1) \end{aligned} \right\}. \quad (16)$$

The elements of the density matrix are expressed as:

$$P_{tu}^1 = \sum_{i=1}^M 2 (C_{it}^{*1} \cdot C_{iu}^0 + C_{it}^{*0} \cdot C_{iu}^1). \quad (17)$$

Then, the correction of the density matrix in first order requires C_i^I calculation. The technique consists of developing C_i^I on a basis of eigenvectors of zero order $\{C_j^0\}$:

$$C_i^1 = \sum_{j=1}^n a_{ij}^1 \cdot C_j^0. \quad (18)$$

All $\{C_j^0\}$ are known as the corresponding eigenvectors of the unperturbed system and the knowledge of all $\{a_{ij}^1\}$ determines fully C_i^I .

Determination of coefficients $\{a_{ij}^1\}$

Substituting (18) in (14.a) gives the form:

$$\left. \begin{aligned} & F^1 C_i^0 + F^0 \sum_{j=1}^n a_{ij}^1 C_j^0 - \\ & \left(e_i^1 S^0 C_i^0 + e_i^0 S^1 C_i^0 + e_i^0 S^0 \sum_{j=1}^n a_{ij}^1 C_j^0 \right) \end{aligned} \right\} = 0.$$

Multiplying the left expression by C_k^{+0} and with linearity and hermitic properties of F^0 and S^0 , we obtain:

$$\left. \begin{aligned} & F_{ki}^1 + \sum_{j=1}^n a_{ij}^1 e_j^0 \delta_{kj} - \\ & \left(e_i^1 \delta_{ki} + e_i^0 S_{ki}^1 + \sum_{j=1}^n e_i^0 a_{ij}^1 \delta_{kj} \right) \end{aligned} \right\} = 0$$

Taking into account the following relations:

$$\begin{cases} F^0 C_j^0 = e_j^0 S^0 C_j^0 \\ C_i^{+0} S^0 C_j^0 = \delta_{ij} \\ F_{ik}^1 = C_i^{+0} F^1 C_k^0 \\ S_{ik}^1 = C_i^{+0} S^1 C_k^0 \end{cases}$$

we can write:

$$(F_{ki}^1 - e_i^0 S_{ki}^1) + a_{ik}^1 (e_k^0 - e_i^0) - e_i^1 \delta_{ki} = 0.$$

We have two options for consideration by the indices i and k .

When $i \neq k$ ($\delta_{ki} = 0$), then:

$$\begin{cases} a_{ik}^1 = \frac{F_{ki}^1 - e_i^0 S_{ki}^1}{e_i^0 - e_k^0} \\ C_k^1 = \sum_{i=1, i \neq k}^n a_{ik}^1 C_i^0 \end{cases}$$

If $i = k$ ($\delta_{ki} = 1$), we obtain the previous expression (15).

Applying the relation between $\{a_{ik}^1\}$ with the decomposition of orthonormality condition (14.b) in the first order of full basis set, we obtain:

$$a_{ij}^{*1} + a_{ji}^1 = -S_{ij}^1 \quad i \neq j; \quad (19.a)$$

$$a_{ii}^{*1} + a_{ii}^1 = -S_{ii}^1 \quad i = j. \quad (19.b)$$

Determination of the matrix P^1

First-order ($m = 1$) correction of the density matrix P is expressed by:

$$P_{rs}^1 = \sum_{i=1}^M 2(C_{ir}^{*1} C_{is}^0 + C_{ir}^{*0} C_{is}^1).$$

The components r and s of the vector C_i^1 are given by $C_{ir}^1 = \sum_{j=1}^n a_{ij}^1 C_{jr}^0$ and $C_{is}^1 = \sum_{j=1}^n a_{ij}^1 C_{js}^0$; in P_{rs}^1 we obtain a new expression:

$$P_{rs}^1 = \sum_{i=1}^M \sum_{j=1}^n 2(a_{ij}^{*1} C_{jr}^{*0} C_{is}^0 + a_{ij}^1 C_{ir}^{*0} C_{js}^0).$$

The relationship (19.a) allows to write $a_{ji}^{*1} = -(a_{ji}^1 + S_{ij}^1)$ and the expression above becomes:

$$P_{rs}^1 = \sum_{i=1}^M \sum_{j=1}^n 2 \left(-a_{ji}^1 C_{jr}^{*0} C_{is}^0 - S_{ij}^1 C_{jr}^{*0} C_{is}^0 + a_{ij}^1 C_{ir}^{*0} C_{js}^0 \right).$$

Finally, after some transformations, the correction to the first order of the matrix density P is given by the following form:

$$\begin{aligned} P^1 = & - \left[\sum_{i=1}^M 2 C_i^{+0} S_{ii}^1 C_i^0 + \sum_{i \neq j}^M 2 (C_j^{+0} S_{ij}^1 C_i^0 + C_i^{+0} S_{ji}^1 C_j^0) \right] + \\ & \sum_{i=1}^M \sum_{j=M+1}^n 2 \left[\frac{F_{ij}^1 - e_i^0 S_{ij}^1}{e_i^0 - e_j^0} C_j^{+0} C_i^0 + \frac{F_{ji}^1 - e_i^0 S_{ji}^1}{e_i^0 - e_j^0} C_i^{+0} C_j^0 \right] \\ P_{rs}^1 = & - \left[\sum_{i=1}^M 2 C_{ir}^{*0} C_{is}^0 S_{ii}^1 + \sum_{i \neq j}^M 2 (S_{ij}^{*0} C_{jr}^0 C_{is}^0 + S_{ji}^1 C_{ir}^{*0} C_{js}^0) \right] + \\ & \sum_{i=1}^M \sum_{j=M+1}^n 2 \left[\frac{F_{ij}^1 - e_i^0 S_{ij}^1}{e_i^0 - e_j^0} C_{jr}^{*0} C_{is}^0 + \frac{F_{ji}^1 - e_i^0 S_{ji}^1}{e_i^0 - e_j^0} C_{ir}^{*0} C_{js}^0 \right] \end{aligned} \quad (20)$$

The relations in expression (20) show that the elements of P^1 are expressed in terms of those of F^1 which depend themselves on P^1 according to relations (16).

The resolution process is to initialize the matrix density to the first order with $P^1 = 0$, which allows us to calculate in the first round $F^1 = h^1$. P^1 is determined by the expression (20) which is then used to calculate $G^1(P^1)$ then F^1 . The iterative process is thus repeated until the system is in coherence.

Expression of F^I

With $F_{ij}^I = C_i^{+0} F^I C_j^0$ and $F^I = h^I + G^I$, then:

$$F_{ij}^I = \sum_{r=1}^n \sum_{s=1}^n C_{ir}^{*0} (h_{rs}^1 + G_{rs}^1) C_{js}^0.$$

Developing $G_{rs} = \sum_{t=1}^n \sum_{u=1}^n P_{tu} \cdot g_{rstu}$ in terms of the first order yields:

$$G_{rs}^1 = \sum_{t=1}^n \sum_{u=1}^n P_{tu}^0 \cdot g_{rstu}^1 + \sum_{t=1}^n \sum_{u=1}^n P_{tu}^1 \cdot g_{rstu}^0. \quad (21)$$

Defining:

$$\bar{G}_{rs}(P^0, g^1) = \sum_{t=1}^n \sum_{u=1}^n P_{tu}^0 \cdot g_{rstu}^1 \quad (21.a)$$

$$\bar{\bar{G}}_{rs}^1(P^1) = \sum_{t=1}^n \sum_{u=1}^n P_{tu}^1 \cdot g_{rstu}^0, \quad (21.b)$$

eq. (21) becomes: $G_{rs}^1 = \bar{G}_{rs}^1(P^0, g^1) + \bar{\bar{G}}_{rs}^1(P^1)$.

Then

$$F_{ij}^1 = \left\{ \sum_{r=1}^n \sum_{s=1}^n C_{ir}^{*0} C_{js}^0 \left[h_{rs}^1 + \bar{G}_{rs}^1(P^0, g^1) + \bar{\bar{G}}_{rs}^1(P^1) \right] \right\}.$$

So, we can write:

$$F_{ij}^1 = C_i^{+0} \left[h^1 + \bar{G}^1(P^0, g^1) + \bar{\bar{G}}^1(P^1) \right] C_j^0.$$

Taking into account the relations $C_i^{+0} h^1 C_j^0 = h_{ij}^1$, $C_i^{+0} \bar{G}^1 C_j^0 = \bar{G}_{ij}^1$ and $C_i^{+0} \bar{\bar{G}}^1 C_j^0 = \bar{\bar{G}}_{ij}^1$, we can write:

$$F_{ij}^1 = h_{ij}^1 + \bar{G}_{ij}^1 + \bar{\bar{G}}_{ij}^1. \quad (22)$$

Expression of the electronic energy E^I

The expressions of E_1^I and E_2^I derived from (7.a) and (7.b) are as follows:

$$E_1^I = \sum_{i=1}^M 2(h_{ii}^1 + C_i^{+1} h^0 C_i^0 + C_i^{+0} h^0 C_i^1); \quad (23.a)$$

$$E_2^I = \left\{ \sum_{i=1}^M (C_i^{+0} G^0 C_i^1 + C_i^{+1} G^0 C_i^0) + \sum_{i=1}^M \sum_{r=1}^n \sum_{s=1}^n C_{ir}^{*0} G_{rs}^1 C_{is}^0 \right\}, \quad (23.b)$$

with:

$$E^I = E_1^I + E_2^I. \quad (23)$$

In developing $C_i^{+0} h^0 C_i^1 + C_i^{+1} h^0 C_i^0$ and taking into account that h^0 is hermetic, we have:

$$\left\{ \begin{aligned} &C_i^{+0} h^0 C_i^1 + C_i^{+1} h^0 C_i^0 = \\ &e_i^0 (C_i^{+0} S^0 C_i^1 + C_i^{+1} S^0 C_i^0) \\ &- (C_i^{+0} G^0 C_i^1 + C_i^{+1} G^0 C_i^0) \end{aligned} \right\}.$$

After the relationship of ortho-normalization at first order, we can write by replacing in expression (23.a):

$$\left\{ \begin{aligned} E_1^I &= \sum_{i=1}^M 2(h_{ii}^1 - e_i^0 S_{ii}^1) \\ &- \sum_{i=1}^M 2(C_i^{+0} G^0 C_i^1 + C_i^{+1} G^0 C_i^0) \end{aligned} \right\}. \quad (23.c)$$

Replacing expressions (23.c) and (23.b) in (23), we obtain:

$$\left\{ \begin{aligned} E^I &= \sum_{i=1}^M 2(h_{ii}^1 - e_i^0 S_{ii}^1) \\ &- \sum_{i=1}^M (C_i^{+0} G^0 C_i^1 + C_i^{+1} G^0 C_i^0) \\ &+ \sum_{i=1}^M \sum_{r=1}^n \sum_{s=1}^n C_{ir}^{*0} G_{rs}^1 C_{is}^0 \end{aligned} \right\}. \quad (24)$$

Taking:

$$X = \sum_{i=1}^M \sum_{r=1}^n \sum_{s=1}^n C_{ir}^{*0} G_{rs}^1 C_{is}^0 \quad (25)$$

and knowing the relation:

$$G_{rs}^1 = \sum_{j=1}^M \sum_{t=1}^n \sum_{u=1}^n 2 \left(\begin{aligned} &C_{jt}^{*1} C_{ju}^0 g_{rstu}^0 \\ &+ C_{jt}^{*0} C_{ju}^1 g_{rstu}^0 \\ &+ C_{jt}^{*0} C_{ju}^0 g_{rstu}^1 \end{aligned} \right),$$

and replacing in (25), we will have:

$$X = \sum_{i=1}^M \sum_{j=1}^M \sum_{r=1}^n \sum_{s=1}^n \sum_{t=1}^n \sum_{u=1}^n 2 C_{ir}^{*0} C_{is}^0 \left(\begin{aligned} &C_{jt}^{*1} C_{ju}^0 g_{rstu}^0 \\ &+ C_{jt}^{*0} C_{ju}^1 g_{rstu}^0 \\ &+ C_{jt}^{*0} C_{ju}^0 g_{rstu}^1 \end{aligned} \right). \quad (26)$$

This relationship is divided into three terms: $X1$, $X2$ and $X3$.

$$X_1 = \sum_{i,j}^M \sum_{rstu}^n 2C_{ir}^{*0} C_{is}^0 C_{jt}^{*1} C_{ju}^0 g_{rstu}^0 ; \quad (26.a)$$

$$X_2 = \sum_{i,j}^M \sum_{rstu}^n 2C_{ir}^{*0} C_{is}^0 C_{jt}^{*0} C_{ju}^1 g_{rstu}^0 ; \quad (26.b)$$

$$X_3 = \sum_{i,j}^M \sum_{rstu}^n 2C_{ir}^{*0} C_{is}^0 C_{jt}^{*0} C_{ju}^1 g_{rstu}^1 . \quad (26.c)$$

In performing a permutation of indices according to $r \leftrightarrow t$, $s \leftrightarrow u$, $i \leftrightarrow j$ and knowing the property of indiscernible electrons ($g_{turs}^0 = g_{rstu}^0$) and through the definitions presented, we obtain:

$$X_1 = \sum_{i=1}^M C_i^{+1} G^0 C_i^0 ; \quad (27.a)$$

$$X_2 = \sum_{i=1}^M C_i^{+0} G^0 C_i^1 ; \quad (27.b)$$

$$X_3 = \sum_{i=1}^M C_i^{+0} \bar{G}^1 C_i^0 . \quad (27.c)$$

The relationship (26) becomes:

$$X = \sum_{i=1}^M \left(C_i^{+1} G^0 C_i^0 + C_i^{+0} G^0 C_i^1 + C_i^{+0} \bar{G}^1 C_i^0 \right).$$

Replacing this expression in (24), we obtain:

$$E^1 = \sum_{i=1}^M \left[2 \left(h_{ii}^1 - e_i^0 S_{ii}^1 \right) + \bar{G}_{ii}^1 \right] . \quad (28.a)$$

And in view of a matrix sense:

$$E^1 = \sum_{i=1}^M 2C_i^{+0} \left(h^1 - e_i^0 S^1 + \frac{1}{2} \bar{G}^1 \right) C_i^0 . \quad (28.b)$$

Expression of energy of first order on a basis LCAO

The expression (28.b) of energy E^1 can be rewritten as:

$$E^1 = \left\{ \begin{aligned} & \sum_{i=1}^M 2C_i^{+0} h^1 C_i^0 \\ & + \sum_{i=1}^M C_i^{+0} \bar{G}^1 C_i^0 \\ & - \sum_{i=1}^M 2e_i^0 C_i^{+0} S^1 C_i^0 \end{aligned} \right\} .$$

The term $C_i^{+0} h^1 C_i^0$ is a scalar product which develops according to:

$$C_i^{+0} h^1 C_i^0 = \sum_{r=1}^n \sum_{s=1}^n C_{ir}^{*0} h_{rs}^1 C_{is}^0 .$$

Then, applying this development to all of the terms, we have:

$$E^1 = \left\{ \begin{aligned} & \sum_{r=1}^n \sum_{s=1}^n h_{rs}^1 \left(\sum_{i=1}^M 2C_{ir}^{*0} C_{is}^0 \right) \\ & + \frac{1}{2} \sum_{r=1}^n \sum_{s=1}^n \bar{G}_{rs}^1 \left(\sum_{i=1}^M 2C_{ir}^{*0} C_{is}^0 \right) \\ & - \sum_{r=1}^n \sum_{s=1}^n S_{rs}^1 \left(\sum_{i=1}^M 2C_{ir}^{*0} C_{is}^0 e_i^0 \right) \end{aligned} \right\} .$$

Introducing:

$$Q_{rs}^0 = \sum_{i=1}^M 2C_{ir}^{*0} C_{is}^0 e_i^0 \quad (29)$$

and knowing that $P_{rs}^0 = \sum_{i=1}^M 2C_{ir}^{*0} C_{is}^0$, we obtain finally:

$$E^1 = \sum_{r=1}^n \sum_{s=1}^n \left[P_{rs}^0 \left(h_{rs}^1 + \frac{1}{2} \bar{G}_{rs}^1 \right) - Q_{rs}^0 S_{rs}^1 \right] . \quad (30)$$

Conclusion

In this work, we developed a new formalism of the McWeeny perturbation theory for expressing the first-order energy correction under external perturbation in the LCAO scheme.

The dependence of the LCAO basis on an external perturbation was taken into account and treated as a perturbation amending the basis set LCAO.

We have established the expressions of the first-order perturbed energies, and our results show that McWeeny approach is a particular case of our global formalism.

Annex: Particularities related to an applied external magnetic field

In the presence of an external perturbation represented by a magnetic field $\vec{B}$, the basis set is built on an ensemble of GIAO (Gauge Invariant Atomic Orbital), proposed by London [14], and expressed as follows:

$$\chi_{k(K)}(\vec{\rho}_K, \vec{B}) = \phi_{k(K)}(\vec{\rho}_K) \eta_{k(K)}(\vec{\rho}_K, \vec{B}) ;$$

where $\chi_{k(K)}(\vec{\rho}_K, \vec{B})$ and $\phi_{k(K)}(\vec{\rho}_K)$ represent respectively the atomic orbital in presence and in absence of perturbation, centered on the K nucleus, and $\eta_{k(K)}(\vec{\rho}_K, \vec{B})$ the term introduced by London defined as:

$$\eta_{k(K)}(\vec{\rho}_K, \vec{B}) = \exp\left\{-\frac{ie}{\hbar c} \cdot \vec{A}_K \cdot \vec{r}\right\},$$

where $\vec{r}$ represents the position vector of the electron compared with an origin, $\vec{\rho}_K = \vec{r} - \vec{R}_K$ is its position vector compared with the K nucleus and $\vec{A}_K = \frac{1}{2} \vec{B} \wedge \vec{R}_K$ signifies the potential-vector on this nucleus, centered on $\vec{R}_K$.

On the other hand, for a weak perturbation, one knows that the energy can be developed in Mac-Laurin-Taylor's series, according to:

$$E = E^0 + E^I + E^2 + \dots$$

where E^0 , E^I , E^2 ... represent respectively the unperturbed energy and the first, second, ... etc perturbed energies.

The size of the first perturbation corresponds to the components of magnetic dipolar moment and is defined as follows:

$$\mu_u = -\left(\frac{\partial E}{\partial B_u}\right)_{B_u=0}.$$

The label u means one of the three orientations of space x , y or z .

References

- [1] Roothaan, C.C.J., Rev. Phys. Mod., 23(1) (1951) 69.
- [2] Roothaan, C.C.J., Rev. Phys. Mod., 32(2) (1960) 179.
- [3] Malykhanov, Y.B., Meshkov, V.V. and Chadin, R.M., Journal of Applied Spectroscopy, 7 (2003) 5.
- [4] Dalgarno, A., London, Proc. Roy. Soc. A, 251 (1959) 282.
- [5] Stiehler, J. and Hinze, J., J. Phys. B, 28 (1995) 4055.
- [6] Malykhanov, Y.B. and Pravosudov, R.N., Prikl. Spektrosk. Zh., 67(1) (2000) 5.
- [7] Stiehler, J. and Hinze, J., J. Phys. B, 28 (1995) 4071.
- [8] Brattsev, V.F. and Khodyreva, N.V., Opt. Spektrosk., 50(2) (1981) 22.
- [9] Brattsev, V.F. and Khodyreva, N.V., Opt. Spektrosk., 54(5) (1983) 927.
- [10] Stewart, R.F., Mol. Phys., 30(4) (1975) 1288.
- [11] Malykhanov, Y.B., Meshkov, V.V. and Chadin, R.M., Prikl. Spektrosk. Zh., 70(5) (2003) 588.
- [12] Van Vleck, J.H., Electric and Magnetic Susceptibilities, (Oxford University Press, Oxford, 1932) 275.
- [13] McWeeny, R., Phys. Rev., 126 (1962) 1034.
- [14] London, F., J. Phys. Radium, 8 (1937) 397.