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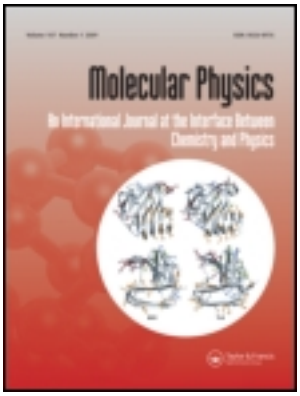

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SCF theory for multiple perturbations

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SCF theory for multiple perturbations

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A fully coupled SCF perturbation theory is developed in matrix form for any number of simultaneous perturbations. Explicit expressions are given for all energy terms up to fourth order in the perturbation parameters. In succeeding papers these expressions are used to produce expressions for and values of several molecular properties dependent upon the simultaneous application of electric and magnetic fields.

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1. INTRODUCTION

In recent years many forms of self-consistent perturbation theory have been developed, and have been applied in the calculation of various atomic and molecular properties. In this paper we consider the simultaneous application of several perturbations using the matrix formulation given by McWeeny [1] and Dierckson and McWeeny [2] to obtain explicit multiple-perturbation expansions up to third and fourth order in the perturbation parameters. The theory, which is ' fully coupled ' in the usual terminology (see, for example, [3]), is applied assuming a closed-shell ground state, but may be extended to the open-shell case along the lines of McWeeny and Dierckson [4]. Applications have been made to the calculation of electric polarizabilities and hyperpolarizabilities [5], to nuclear magnetic shielding [6] and to molecular dipole magnetizability [7]. Further applications will be reported in detail in the succeeding papers.

2. BASIS OF THE METHOD

We summarize briefly the basic equations, using a familiar matrix notation (see, for example, reference [8]). The doubly occupied orbitals $\psi_1, \psi_2, \ldots \psi_n$ are expressed in terms of the basis functions $\phi_1, \phi_2, \ldots \phi_m$ (assumed orthonormal) by

$$\boldsymbol{\psi} = \boldsymbol{\phi}\mathbf{T}, \tag{2.1}$$

where $\mathbf{T}$ is an $m \times n$ matrix. The orthonormality condition on the ϕ's is equivalent to an idempotency condition on the matrix

$$\mathbf{R} = \mathbf{T}\mathbf{T}^{\dagger}. \tag{2.2}$$

Thus

$$\mathbf{R}^2 = \mathbf{R} \tag{2.3}$$

and $\mathbf{R}$ defines a projection operator onto the subspace spanned by the n occupied orbitals.

The Hartree–Fock equations may be written in the form [7]

$$\mathbf{hR}-\mathbf{Rh}=\mathbf{0}, \tag{2.4}$$

where $\mathbf{h}$ is the matrix of the Hartree–Fock hamiltonian. Explicitly

$$\mathbf{h}=\mathbf{f}+\mathbf{G}(\mathbf{R}), \tag{2.5}$$

in which $\mathbf{f}$ is the bare-nuclear term and $\mathbf{G}$ is the electron interaction matrix, which depends on the electron density and hence on $\mathbf{R}$.

Quantities referring to the unperturbed system will be labelled by a superscript zero and it will be assumed that $\mathbf{h}^{(0)}$ and $\mathbf{R}^{(0)}$ satisfy (2.4). It will be sufficient to consider a one-electron perturbation, in which

$$\mathbf{f}^{(0)}\rightarrow\mathbf{f}=\mathbf{f}^{(0)}+\lambda\mathbf{f}^{(1)}+\lambda^2\,\mathbf{f}^{(2)}+\dots\,. \tag{2.6}$$

The matrices $\mathbf{h}$ and $\mathbf{R}$ may then be expanded as power series ;

$$\left.\begin{aligned}\mathbf{h}&=\mathbf{h}^{(0)}+\lambda\mathbf{h}^{(1)}+\lambda^2\,\mathbf{h}^{(2)}+\dots\,,\\ \mathbf{R}&=\mathbf{R}^{(0)}+\lambda\mathbf{R}^{(1)}+\lambda^2\,\mathbf{R}^{(2)}+\dots\,.\end{aligned}\right\} \tag{2.7}$$

The perturbation parameter λ is here purely formal, distinguishing terms of different order, and is finally put equal to unity.

The condition (2.3) imposes restrictions on $\mathbf{R}^{(1)}$, $\mathbf{R}^{(2)}$, ... which are conveniently expressed in terms of the ' projections ' of the matrices with respect to the ' occupied ' and ' unoccupied ' subspaces characterized by the projectors $\mathbf{R}_1(=\mathbf{R}^{(0)})$ and $\mathbf{R}_2=\mathbf{1}-\mathbf{R}^{(0)}$. The (ij) projection of a matrix $\mathbf{M}$ is

$$\mathbf{M}_{ij}=\mathbf{R}_i\mathbf{M}\mathbf{R}_j \quad (i,\,j=1,\,2) \tag{2.8}$$

and equality of two matrices implies equality of corresponding projected parts. The use of the projection operator technique in solving equation (2.4) is briefly outlined in the Appendix, where it is shown that $\mathbf{R}^{(1)}$ has only (12) and (21) projections related by a hermitian symmetry requirement and hence that

$$\mathbf{R}^{(1)}=\mathbf{x}+\mathbf{x}^{\dagger},\quad \mathbf{x}=\mathbf{R}_{12}{}^{(1)}. \tag{2.9}$$

The matrix $\mathbf{x}$ is determined by using the first-order condition resulting from (2.4). The most convenient formula for the calculation of $\mathbf{x}$ is

$$\mathbf{x}=\sum_{\substack{K(\mathrm{occ})\\ L(\mathrm{unocc})}}\frac{h_{KL}{}^{(1)}}{\epsilon_K-\epsilon_L}\,\mathbf{c}_K\mathbf{c}_L{}^{\dagger}, \tag{2.10}$$

where ϵ_K and $\mathbf{c}_K$ are the Kth eigenvalue and eigenvector of the unperturbed Hartree–Fock hamiltonian $\mathbf{h}^{(0)}$ and

$$h_{KL}{}^{(1)}=\mathbf{c}_K{}^{\dagger}\,\mathbf{h}^{(1)}\,\mathbf{c}_L=\mathbf{c}_K{}^{\dagger}[\mathbf{f}^{(1)}+\mathbf{G}(\mathbf{R}^{(1)})]\mathbf{c}_L. \tag{2.11}$$

Since $\mathbf{h}^{(1)}$ depends on $\mathbf{R}^{(1)}\,(=\mathbf{x}+\mathbf{x}^{\dagger})$ it is necessary to obtain $\mathbf{x}$ from (2.10) by iteration ; in previous work, convergence has been found to be rapid.

The forms of $\mathbf{R}^{(2)}$ and $\mathbf{R}^{(3)}$ are found to be, listing their projected parts in the order (11), (12), (21), (22) :

$$\mathbf{R}^{(2)}=-\mathbf{x}\mathbf{x}^{\dagger}+\mathbf{y}+\mathbf{y}^{\dagger}+\mathbf{x}^{\dagger}\,\mathbf{x}, \tag{2.12}$$

$$\mathbf{R}^{(3)}=-(\mathbf{x}\mathbf{y}^{\dagger}+\mathbf{y}\mathbf{x}^{\dagger})+\mathbf{z}+\mathbf{z}^{\dagger}+(\mathbf{x}^{\dagger}\,\mathbf{y}+\mathbf{y}^{\dagger}\,\mathbf{x}). \tag{2.13}$$

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The (12) and (21) components in each successive order are determined by a single new quantity; $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ for first, second and third order. The (11) and (22) components are determined by the 'irreducible' components of *lower* order and are associated with renormalization of the wavefunction. In going to fourth order in the energy, we shall need only the (11) and (22) components of $\mathbf{R}^{(4)}$; these are

$$\left.\begin{aligned}\mathbf{R}_{11}{}^{(4)} &= -(\mathbf{x}\mathbf{x}^\dagger\,\mathbf{x}\mathbf{x}^\dagger + \mathbf{x}\mathbf{z}^\dagger + \mathbf{y}\mathbf{y}^\dagger + \mathbf{z}\mathbf{x}^\dagger),\\ \mathbf{R}_{22}{}^{(4)} &= (\mathbf{x}^\dagger\,\mathbf{x}\mathbf{x}^\dagger\,\mathbf{x} + \mathbf{x}^\dagger\,\mathbf{z} + \mathbf{y}^\dagger\,\mathbf{y} + \mathbf{z}^\dagger\,\mathbf{x}).\end{aligned}\right\} \tag{2.14}$$

The (12) components, $\mathbf{y}$ and $\mathbf{z}$, of $\mathbf{R}^{(2)}$ and $\mathbf{R}^{(3)}$ are determined from expressions similar to (2.10). For example

$$\mathbf{y} = \mathbf{R}_{12}{}^{(2)} = \sum_{\substack{K(\mathrm{occ})\\ L(\mathrm{unocc})}} \frac{M_{KL}{}^{(2)}}{\epsilon_K - \epsilon_L}\,\mathbf{c}_K\mathbf{c}_L{}^\dagger. \tag{2.15}$$

The general form of $\mathbf{M}^{(k)}$ is known [1, 2] and gives for $k=2$

$$M_{KL}{}^{(2)} = \mathbf{c}_K{}^\dagger[\mathbf{h}^{(2)} + \mathbf{x}\mathbf{h}^{(1)} - \mathbf{h}^{(1)}\mathbf{x}]\mathbf{c}_L. \tag{2.16}$$

The required matrix $\mathbf{y}$ follows by iteration, in exactly the same way as $\mathbf{x}$. When working only up to fourth order in the energy the matrix $\mathbf{z}$ will not be required.

The energy $E^{(k)}$ is obtained by writing

$$E = 2\,\mathrm{tr}\,\mathbf{h}'\mathbf{R} \quad (\mathbf{h}' = \mathbf{f} + \tfrac{1}{2}\mathbf{G}) \tag{2.17}$$

and separating out the terms of order k. In this way we obtain [1, 2, 5], after considerable re-arrangement (and use of the equations satisfied by $\mathbf{x}$ and $\mathbf{y}$),

$$E^{(1)} = 2\,\mathrm{tr}\,\mathbf{f}^{(1)}\,\mathbf{R}^{(0)}, \tag{2.18}$$

$$E^{(2)} = 2\,\mathrm{tr}\,[\mathbf{f}^{(2)}\,\mathbf{R}^{(0)} + \tfrac{1}{2}\mathbf{f}^{(1)}\,\mathbf{R}^{(1)}], \tag{2.19}$$

$$E^{(3)} = 2\,\mathrm{tr}\,[\mathbf{f}^{(3)}\,\mathbf{R}^{(0)} + \mathbf{f}^{(2)}\,\mathbf{R}^{(1)}] + 2\,\mathrm{tr}\,[\mathbf{h}^{(1)}(\mathbf{R}_{11}{}^{(2)} + \mathbf{R}_{22}{}^{(2)})], \tag{2.20}$$

$$\begin{aligned}E^{(4)} = 2\,\mathrm{tr}\,[&\mathbf{f}^{(4)}\,\mathbf{R}^{(0)} + \mathbf{f}^{(3)}\,\mathbf{R}^{(1)} + \tfrac{1}{2}\mathbf{f}^{(2)}\,\mathbf{R}^{(2)}] + 2\,\mathrm{tr}\,[\tfrac{1}{2}\mathbf{h}^{(2)}(\mathbf{R}_{11}{}^{(2)} + \mathbf{R}_{22}{}^{(2)})\\ &+ \tfrac{1}{2}\mathbf{h}^{(1)}(\mathbf{R}_{11}{}^{(3)} + \mathbf{R}_{22}{}^{(3)}) + \mathbf{h}^{(0)}(-\mathbf{R}_{11}{}^{(2)}\,\mathbf{R}_{11}{}^{(2)} + \mathbf{R}_{22}{}^{(2)}\,\mathbf{R}_{22}{}^{(2)})].\end{aligned} \tag{2.21}$$

The final terms in (2.20) and (2.21) arise from the lower-order re-normalization corrections, and the resultant expressions can be written in various alternative forms. As in standard perturbation theory, the nth order wavefunction (and hence the irreducible parts of $\mathbf{R}^{(n)}$) determines the energy to order $(2n+1)$.

3. Extension to multiple perturbations

The simplest multiple perturbation would be of the form

$$\mathbf{f}^{(1)} = a\mathbf{f}^a + b\mathbf{f}^b + c\mathbf{f}^c + \ldots,$$

where a, b, c are any convenient perturbation parameters (either 'physical' such as field components, or 'formal' and ultimately set equal to unity). In some cases (e.g. in discussing diamagnetism) the full hamiltonian contains terms quadratic in a perturbation parameter (e.g. in B^2) and the most general perturbed f matrix would be written

$$\mathbf{f} = \mathbf{f}^{(0)} + (a\mathbf{f}^a + b\mathbf{f}^b + \ldots) + (a^2\,\mathbf{f}^{a^2} + b^2\,\mathbf{f}^{b^2} + \ldots + ab\mathbf{f}^{ab} + \ldots) + \ldots.$$

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This is of the standard form (2.6), for $\lambda = 1$, with the identification

$$\mathbf{f}^{(1)} = a\mathbf{f}^{a} + b\mathbf{f}^{b} + \dots, \tag{3.1}$$

$$\mathbf{f}^{(2)} = a^2\,\mathbf{f}^{a^2} + b^2\,\mathbf{f}^{b^2} + \dots + ab\mathbf{f}^{ab} + \dots, \tag{3.2}$$

$$\mathbf{f}^{(3)} = a^3\,\mathbf{f}^{a^3} + b^3\,\mathbf{f}^{b^3} + \dots + a^2b\mathbf{f}^{a^2b} + \dots + abc\mathbf{f}^{abc} + \dots, \tag{3.3}$$

and it is therefore possible to take over all the previous results, separating various types and orders of perturbation in terms of corresponding powers of a, b, c. It should be noted that in the above equations the order of the superscripts is irrelevant; $ab\mathbf{f}^{ab}$ is the entire perturbation term linear in a and b, and there is no additional $\mathbf{f}^{ba}$; similarly $\mathbf{f}^{a^2b}$ is not accompanied by other terms such as $\mathbf{f}^{aba}$. An alternative but somewhat less explicit notation is to be used in subsequent papers. This uses a numerical index to denote the order of each perturbation parameter with the following correspondence:

$$\mathbf{f}^{a} \equiv \mathbf{f}^{100\cdot\cdot}, \quad \mathbf{f}^{ab} \equiv \mathbf{f}^{110\cdot\cdot}, \quad \mathbf{f}^{a^2c} \equiv \mathbf{f}^{201\cdot\cdot}, \text{ etc.}$$

The notation of equations (3.1)–(3.3) is more transparent and less cumbersome when presenting the general derivation than the alternative, but the reverse situation prevails in a specific problem with a specified number of perturbations arranged in a defined order.

First we note that $\mathbf{x}$ given by equation (2.10) will break up into a sum of terms which may be determined independently:

$$\mathbf{x} = a\mathbf{x}_a + b\mathbf{x}_b + \dots, \tag{3.4}$$

where

$$\mathbf{x}_a = \sum_{\substack{K(\mathrm{occ})\\ L(\mathrm{unocc})}} \frac{h_{KL}{}^{a}}{\epsilon_K - \epsilon_L}\,\mathbf{c}_K\mathbf{c}_L{}^{\dagger} \tag{3.5}$$

and

$$h_{KL}{}^{a} = \mathbf{c}_K{}^{\dagger}\,\mathbf{h}^{a}\,\mathbf{c}_L = \mathbf{c}_K{}^{\dagger}[\mathbf{f}^{a} + \mathbf{G}(\mathbf{R}^{a})]\mathbf{c}_L. \tag{3.6}$$

Here $\mathbf{R}^{a}$ is the a-dependent term in $\mathbf{x} + \mathbf{x}^{\dagger}$ (i.e. $\mathbf{x}_a + \mathbf{x}_a{}^{\dagger}$) and the iteration thus involves $\mathbf{x}_a$ alone; to first order each perurbation may be treated as if it acted alone. From (3.4), however, we may derive also the quadratic and cubic terms in the energy by substitution in (2.19) and (2.20). The results follow by inspection on picking out the various powers of a, b, c:

1st order:

$$E^{a} = 2\,\mathrm{tr}\,[\mathbf{f}^{a}\,\mathbf{R}^{0}], \tag{3.7}$$

2nd order:

$$E^{a^2} = 2\,\mathrm{tr}\,[\mathbf{f}^{a^2}\,\mathbf{R}^{0} + \tfrac{1}{2}\mathbf{f}^{a}\,\mathbf{R}^{a}], \tag{3.8}$$

$$E^{ab} = 2\,\mathrm{tr}\,[\mathbf{f}^{ab}\,\mathbf{R}^{0} + \tfrac{1}{2}\mathbf{f}^{a}\,\mathbf{R}^{b} + \tfrac{1}{2}\mathbf{f}^{b}\,\mathbf{R}^{a}] \tag{3.9}$$

3rd order:

$$E^{a^3} = 2\,\mathrm{tr}\,[\mathbf{f}^{a^3}\,\mathbf{R}^{0} + \mathbf{f}^{a^2}\,\mathbf{R}^{a}] + 2\,\mathrm{tr}\,[\mathbf{h}^{a}(\mathbf{R}_{11}{}^{a^2} + \mathbf{R}_{22}{}^{a^2})], \tag{3.10}$$

$$E^{a^2b} = 2\,\mathrm{tr}\,[\mathbf{f}^{a^2b}\,\mathbf{R}^{0} + \mathbf{f}^{ab}\,\mathbf{R}^{a} + \mathbf{f}^{a^2}\,\mathbf{R}^{b}] + 2\,\mathrm{tr}\,[\mathbf{h}^{a}(\mathbf{R}_{11}{}^{ab} + \mathbf{R}_{22}{}^{ab}) + \mathbf{h}^{b}(\mathbf{R}_{11}{}^{a^2} + \mathbf{R}_{22}{}^{a^2})], \tag{3.11}$$

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$$E^{abc} = 2\ \mathrm{tr}\ [\mathbf{f}^{abc}\ \mathbf{R}^0 + \mathbf{f}^{ab}\ \mathbf{R}^c + \mathbf{f}^{ac}\ \mathbf{R}^b + \mathbf{f}^{bc}\ \mathbf{R}^a] + 2\ \mathrm{tr}\ [\mathbf{h}^a(\mathbf{R}_{11}{}^{bc} + \mathbf{R}_{22}{}^{bc}) + \mathbf{h}^b(\mathbf{R}_{11}{}^{ac} + \mathbf{R}_{22}{}^{ac}) + \mathbf{h}^c(\mathbf{R}_{11}{}^{ab} + \mathbf{R}_{22}{}^{ab})]. \quad (3.12)$$

It is evident from (2.13) that the (11) and (22) components of the second-order density changes are given by

$$\left.\begin{aligned} \mathbf{R}_{11}{}^{ab} &= -(\mathbf{x}_a\mathbf{x}_b{}^\dagger + \mathbf{x}_b\mathbf{x}_a{}^\dagger), \\ \mathbf{R}_{22}{}^{ab} &= \mathbf{x}_a{}^\dagger\ \mathbf{x}_b + \mathbf{x}_b{}^\dagger\ \mathbf{x}_a. \end{aligned}\right\} \quad (3.13)$$

The above results are valid for any number of simultaneous perturbations.

To obtain the fourth and fifth-order terms we need the second-order matrix $\mathbf{y}$ in (2.13). This is determined from (2.15) and has the form

$$\mathbf{y} = a^2\ \mathbf{y}_{a^2} + b^2\ \mathbf{y}_{b^2} + \ldots + ab\mathbf{y}_{ab} + \ldots, \quad (3.14)$$

where $\mathbf{y}_{a^2}$ and $\mathbf{y}_{b^2}$ are each obtained exactly as for one perturbation only, but there is now an extra ' cross term ' for each pair :

$$\mathbf{y}_{ab} = \sum_{\substack{K(\mathrm{occ}) \\ L(\mathrm{unocc})}} \frac{M_{KL}{}^{ab}}{\epsilon_K - \epsilon_L}\ \mathbf{c}_K\mathbf{c}_L{}^\dagger. \quad (3.15)$$

From (2.16) it is seen that iteration requires knowledge of the first-order quantities $\mathbf{x}_a$ and $\mathbf{x}_b$, for

$$M_{KL}{}^{ab} = \mathbf{c}_K{}^\dagger[\mathbf{h}^{ab} + \mathbf{x}_a\mathbf{h}^b + \mathbf{x}_b\mathbf{h}^a - \mathbf{h}^b\mathbf{x}_a - \mathbf{h}^a\ \mathbf{x}_b]\mathbf{c}_L. \quad (3.16)$$

The iteration determines $\mathbf{y}_{ab}$, which occurs only in the term $\mathbf{h}^{ab}$, and proceeds exactly as in other cases.

The fourth-order energy change follows on substituting for the various $\mathbf{R}$ matrices in (2.21) and picking out terms in given powers of a, b and c. Thus we find :

$$E^{a^4} = 2\ \mathrm{tr}\ [\mathbf{f}^{a^4}\ \mathbf{R}^0 + \mathbf{f}^{a^3}\ \mathbf{R}^a + \tfrac{1}{2}\mathbf{f}^{a^2}\ \mathbf{R}^{a^2}] + 2\ \mathrm{tr}\ [\tfrac{1}{2}\mathbf{h}^{a^2}(\mathbf{R}_{11}{}^{a^2} + \mathbf{R}_{22}{}^{a^2}) + \tfrac{1}{2}\mathbf{h}^a(\mathbf{R}_{11}{}^{a^3} + \mathbf{R}_{22}{}^{a^3}) + \mathbf{h}^0(-\mathbf{R}_{11}{}^{a^2}\ \mathbf{R}_{11}{}^{a^2} + \mathbf{R}_{22}{}^{a^2}\ \mathbf{R}_{22}{}^{a^2})] \quad (3.17)$$

$$\begin{aligned} E^{a^3b} = {} & 2\ \mathrm{tr}\ [\mathbf{f}^{a^3b}\ \mathbf{R}^0 + (\mathbf{f}^{a^3}\ \mathbf{R}^b + \mathbf{f}^{a^2b}\ \mathbf{R}^a) + \tfrac{1}{2}(\mathbf{f}^{a^2}\ \mathbf{R}^{ab} + \mathbf{f}^{ab}\ \mathbf{R}^{a^2})] \\ & + 2\ \mathrm{tr}\ [\tfrac{1}{2}\mathbf{h}^{a^2}(\mathbf{R}_{11}{}^{ab} + \mathbf{R}_{22}{}^{ab}) + \tfrac{1}{2}\mathbf{h}^{ab}(\mathbf{R}_{11}{}^{a^2} + \mathbf{R}_{22}{}^{a^2}) + \tfrac{1}{2}\mathbf{h}^a(\mathbf{R}_{11}{}^{a^2b} + \mathbf{R}_{22}{}^{a^2b}) \\ & + \tfrac{1}{2}\mathbf{h}^b(\mathbf{R}_{11}{}^{a^3} + \mathbf{R}_{22}{}^{a^3}) + \mathbf{h}^0(-\mathbf{R}_{11}{}^{a^2}\ \mathbf{R}_{11}{}^{ab} - \mathbf{R}_{11}{}^{ab}\ \mathbf{R}_{11}{}^{a^2} \\ & \qquad + \mathbf{R}_{22}{}^{a^2}\ \mathbf{R}_{22}{}^{ab} + \mathbf{R}_{22}{}^{ab}\ \mathbf{R}_{22}{}^{a^2})], \end{aligned} \quad (3.18)$$

$$\begin{aligned} E^{a^2b^2} = {} & 2\ \mathrm{tr}\ [\mathbf{f}^{a^2b^2}\ \mathbf{R}^0 + (\mathbf{f}^{a^2b}\ \mathbf{R}^b + \mathbf{f}^{ab^2}\ \mathbf{R}^a) + \tfrac{1}{2}(\mathbf{f}^{a^2}\ \mathbf{R}^{b^2} + \mathbf{f}^{ab}\ \mathbf{R}^{ab} + \mathbf{f}^{b^2}\ \mathbf{R}^{a^2})] \\ & + 2\ \mathrm{tr}\ [\tfrac{1}{2}\mathbf{h}^{a^2}(\mathbf{R}_{11}{}^{b^2} + \mathbf{R}_{22}{}^{b^2}) + \tfrac{1}{2}\mathbf{h}^{ab}(\mathbf{R}_{11}{}^{ab} + \mathbf{R}_{22}{}^{ab}) + \tfrac{1}{2}\mathbf{h}^{b^2}(\mathbf{R}_{11}{}^{a^2} + \mathbf{R}_{22}{}^{a^2}) \\ & + \tfrac{1}{2}\mathbf{h}^a(\mathbf{R}_{11}{}^{ab^2} + \mathbf{R}_{22}{}^{ab^2}) + \tfrac{1}{2}\mathbf{h}^b(\mathbf{R}_{11}{}^{a^2b} + \mathbf{R}_{22}{}^{a^2b}) + \mathbf{h}^0(-\mathbf{R}_{11}{}^{a^2}\ \mathbf{R}_{11}{}^{b^2} \\ & - \mathbf{R}_{11}{}^{b^2}\ \mathbf{R}_{11}{}^{a^2} - \mathbf{R}_{11}{}^{ab}\ \mathbf{R}_{11}{}^{ab} + \mathbf{R}_{22}{}^{a^2}\ \mathbf{R}_{22}{}^{b^2} + \mathbf{R}_{22}{}^{b^2}\ \mathbf{R}_{22}{}^{a^2} \\ & \qquad + \mathbf{R}_{22}{}^{ab}\ \mathbf{R}_{22}{}^{ab})], \end{aligned} \quad (3.19)$$

$$\begin{aligned} E^{a^2bc} = {} & 2\ \mathrm{tr}\ [\mathbf{f}^{a^2bc}\ \mathbf{R}^0 + (\mathbf{f}^{a^2b}\ \mathbf{R}^c + \mathbf{f}^{a^2c}\ \mathbf{R}^b + \mathbf{f}^{abc}\ \mathbf{R}^a) \\ & + \tfrac{1}{2}(\mathbf{f}^{a^2}\ \mathbf{R}^{bc} + \mathbf{f}^{ab}\ \mathbf{R}^{ac} + \mathbf{f}^{ac}\ \mathbf{R}^{ab})] + 2\ \mathrm{tr}\ [\tfrac{1}{2}\mathbf{h}^{a^2}(\mathbf{R}_{11}{}^{bc} + \mathbf{R}_{22}{}^{bc}) \\ & + \tfrac{1}{2}\mathbf{h}^{ab}(\mathbf{R}_{11}{}^{ac} + \mathbf{R}_{22}{}^{ac}) + \tfrac{1}{2}\mathbf{h}^{ac}(\mathbf{R}_{11}{}^{ab} + \mathbf{R}_{22}{}^{ab}) + \tfrac{1}{2}\mathbf{h}^a(\mathbf{R}_{11}{}^{abc}\ \mathbf{R}_{22}{}^{abc}) \\ & + \tfrac{1}{2}\mathbf{h}^b(\mathbf{R}_{11}{}^{a^2c} + \mathbf{R}_{22}{}^{a^2c}) + \tfrac{1}{2}\mathbf{h}^c(\mathbf{R}_{11}{}^{a^2b} + \mathbf{R}_{22}{}^{a^2b}) + \mathbf{h}^0(-\mathbf{R}_{11}{}^{a^2}\ \mathbf{R}_{11}{}^{bc} \\ & - \mathbf{R}_{11}{}^{ab}\ \mathbf{R}_{11}{}^{ac} - \mathbf{R}_{11}{}^{ac}\ \mathbf{R}_{11}{}^{ab} + \mathbf{R}_{22}{}^{a^2}\ \mathbf{R}_{22}{}^{bc} + \mathbf{R}_{22}{}^{ab}\ \mathbf{R}_{22}{}^{ac} \\ & \qquad + \mathbf{R}_{22}{}^{ac}\ \mathbf{R}_{22}{}^{ab})], \end{aligned} \quad (3.20)$$

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Finally

$$\begin{aligned} E^{abcd} = 2\,\mathrm{tr}\,[&\mathbf{f}^{abcd}\,\mathbf{R}^0 + (\mathbf{f}^{abc}\,\mathbf{R}^d + \mathbf{f}^{abd}\,\mathbf{R}^c + \mathbf{f}^{acd}\,\mathbf{R}^b + \mathbf{f}^{bcd}\,\mathbf{R}^a) \\ &+ \tfrac{1}{2}(\mathbf{f}^{ab}\,\mathbf{R}^{cd} + \mathbf{f}^{ac}\,\mathbf{R}^{bd} + \mathbf{f}^{ad}\,\mathbf{R}^{bc} + \mathbf{f}^{bc}\,\mathbf{R}^{ad})] \\ &+ 2\,\mathrm{tr}\,[\tfrac{1}{2}\mathbf{h}^{ab}(\mathbf{R}_{11}{}^{cd} + \mathbf{R}_{22}{}^{cd}) + \tfrac{1}{2}\mathbf{h}^{ac}(\mathbf{R}_{11}{}^{bd} + \mathbf{R}_{22}{}^{bd}) + \ldots(6\text{ terms}) \\ &+ \tfrac{1}{2}\mathbf{h}^{a}(\mathbf{R}_{11}{}^{bcd} + \mathbf{R}_{22}{}^{bcd}) + \tfrac{1}{2}\mathbf{h}^{b}(\mathbf{R}_{11}{}^{acd} + \mathbf{R}_{22}{}^{acd}) + \ldots(4\text{ terms}) \\ &\qquad + \mathbf{h}^0(-\mathbf{R}_{11}{}^{ab}\,\mathbf{R}_{11}{}^{cd} + \mathbf{R}_{22}{}^{ab}\,\mathbf{R}_{22}{}^{cd} + \ldots(6\text{ pairs}))] \end{aligned} \tag{3.21}$$

(The terms not shown arise obviously from the six selections of two pairs from *abcd*, or the four selections of one plus three letters.)

In the above expressions the (11) and (22) components of the density corrections are given by (3.13) together with

$$\left.\begin{aligned} \mathbf{R}_{11}{}^{a^3} &= -(\mathbf{x}_a\mathbf{y}_{a^2}{}^\dagger + \mathbf{y}_a\mathbf{x}_{a^2}{}^\dagger), \\ \mathbf{R}_{22}{}^{a^3} &= (\mathbf{x}_a{}^\dagger\,\mathbf{y}_{a^2} + \mathbf{y}_a{}^\dagger\,\mathbf{x}_{a^2}), \end{aligned}\right\} \tag{3.22}$$

$$\left.\begin{aligned} \mathbf{R}_{11}{}^{a^2b} &= -(\mathbf{x}_a\mathbf{y}_{ab}{}^\dagger + \mathbf{x}_b\mathbf{y}_{a^2}{}^\dagger + \mathbf{y}_a\mathbf{x}_{ab}{}^\dagger + \mathbf{y}_b\mathbf{x}_{ab}{}^\dagger), \\ \mathbf{R}_{22}{}^{a^2b} &= (\mathbf{x}_a{}^\dagger\,\mathbf{y}_{ab} + \mathbf{x}_b{}^\dagger\,\mathbf{y}_{a^2} + \mathbf{y}_a{}^\dagger\,\mathbf{x}_{ab} + \mathbf{y}_b{}^\dagger\,\mathbf{x}_{ab}), \end{aligned}\right\} \tag{3.23}$$

$$\left.\begin{aligned} \mathbf{R}_{11}{}^{abc} &= -(\mathbf{x}_a\mathbf{y}_{bc}{}^\dagger + \mathbf{x}_b\mathbf{y}_{ac}{}^\dagger + \mathbf{x}_c\mathbf{y}_{ab}{}^\dagger + \mathbf{y}_a\mathbf{x}_{bc}{}^\dagger + \mathbf{y}_b\mathbf{x}_{ac}{}^\dagger + \mathbf{y}_c\mathbf{x}_{ab}{}^\dagger), \\ \mathbf{R}_{22}{}^{abc} &= (\mathbf{x}_a{}^\dagger\,\mathbf{y}_{bc} + \mathbf{x}_b{}^\dagger\,\mathbf{y}_{ac} + \mathbf{x}_c{}^\dagger\,\mathbf{y}_{ab} + \mathbf{y}_a{}^\dagger\,\mathbf{x}_{bc} + \mathbf{y}_b{}^\dagger\,\mathbf{x}_{ac} + \mathbf{y}_c{}^\dagger\,\mathbf{x}_{ab}). \end{aligned}\right\} \tag{3.24}$$

In certain special cases (e.g. when there are no independent perturbations of type $\mathbf{f}^{a^2}$, $\mathbf{f}^{ab}$, $\mathbf{f}^{b^2}$, and higher order, and (3.1) represents the whole perturbation) some terms vanish or become equal and reductions occur. Various 'interchange theorems' may then be established. The forms given above, in which the parameters enter in a symmetrical way in each order, are completely general.

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Appendix

On substituting from (2.7) in (2.3) and equating terms of corresponding order we obtain

$$\mathbf{R}^{(0)}\,\mathbf{R}^{(1)} + \mathbf{R}^{(1)}\,\mathbf{R}^{(0)} = \mathbf{R}^{(1)}, \tag{A 1}$$

$$\mathbf{R}^{(0)}\,\mathbf{R}^{(2)} + \mathbf{R}^{(2)}\,\mathbf{R}^{(0)} + \mathbf{R}^{(1)}\mathbf{R}^{(1)} = \mathbf{R}^{(2)}, \tag{A 2}$$

etc. On multiplying from left and right by $\mathbf{R}_1(=\mathbf{R}^{(0)})$ (A 1) gives $2\mathbf{R}_{11}{}^{(1)} = \mathbf{R}_{11}{}^{(1)}$ and hence $\mathbf{R}_{11}{}^{(1)} = \mathbf{0}$. Similarly, use of $\mathbf{R}_2(=\mathbf{1}-\mathbf{R}^{(0)})$ yields $\mathbf{R}_{22}{}^{(1)} = \mathbf{0}$. For the (12) projection, however, we obtain the trivial identity $\mathbf{R}_{12}{}^{(1)} = \mathbf{R}_{12}{}^{(1)} = \mathbf{x}$, say. The hermitian symmetry of R requires $\mathbf{R}_{21}{}^{(1)} = \mathbf{R}_{12}{}^{(1)\dagger}$ and hence

$$\mathbf{R}^{(1)} = \mathbf{x} + \mathbf{x}^\dagger. \tag{A 3}$$

Application of the same technique to the second-order equation (A 2) yields, since $\mathbf{R}^{(1)}\mathbf{R}^{(1)} = \mathbf{x}\mathbf{x}^\dagger + \mathbf{x}^\dagger\,\mathbf{x}$,

$$2\mathbf{R}_{11}{}^{(2)} + \mathbf{x}\mathbf{x}^\dagger = \mathbf{R}_{11}{}^{(2)}$$

and hence $\mathbf{R}_{11}{}^{(2)} = -\mathbf{x}\mathbf{x}^\dagger$. The (22) component is found similarly to be $\mathbf{R}_{22}{}^{(2)} = \mathbf{x}^\dagger\,\mathbf{x}$, while the (12) and (21) components are undetermined except

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that they are hermitian conjugate. Hence

$$\mathbf{R}^{(2)} = -\mathbf{x}\mathbf{x}^{\dagger} + \mathbf{y} + \mathbf{y}^{\dagger} + \mathbf{x}^{\dagger}\,\mathbf{x}. \tag{A 4}$$

Expressions (2.13) and (2.14) are obtained similarly.

The undetermined components, $\mathbf{x}$, $\mathbf{y}$, . . . must be chosen to satisfy (2.4) to each order. Thus, in first order,

$$\mathbf{h}^{(0)}\,\mathbf{R}^{(1)} - \mathbf{R}^{(1)}\,\mathbf{h}^{(0)} + \mathbf{h}^{(1)}\,\mathbf{R}^{(0)} - \mathbf{R}^{(0)}\,\mathbf{h}^{(1)} = \mathbf{0}, \tag{A 5}$$

and (12) projection gives (since $\mathbf{R}^{(0)}$ commutes with $\mathbf{h}^{(0)}$)

$$\mathbf{h}^{(0)}\,\mathbf{x} - \mathbf{x}\mathbf{h}^{(0)} - \mathbf{h}_{12}{}^{(1)} = \mathbf{0}.$$

Now $\mathbf{x}$ may be written in terms of the eigenvectors of $\mathbf{h}^{(0)}$ as

$$\mathbf{x} = \sum_{I,J} A_{IJ}\mathbf{c}_I\mathbf{c}_J{}^{\dagger},$$

where, since only the (12) projection is non-zero, I and J run over occupied and unoccupied orbitals, respectively. Substitution and use of $\mathbf{h}^{(0)}\,\mathbf{c}_I = \epsilon_I\mathbf{c}_I$, yields

$$\sum_{\substack{I(\mathrm{occ})\\ J(\mathrm{unocc})}} A_{IJ}(\epsilon_I - \epsilon_J)\mathbf{c}_I\mathbf{c}_J{}^{\dagger} = \mathbf{h}_{12}{}^{(1)}.$$

Multiplication from left and right by particular eigenvectors, $\mathbf{c}_K{}^{\dagger}$ and $\mathbf{c}_L$ (K occupied, L unoccupied) then fixed A_{JK}. The result is

$$\mathbf{x} = \sum_{\substack{J(\mathrm{occ})\\ L(\mathrm{unocc})}} \frac{h_{KL}{}^{(1)}}{\epsilon_K - \epsilon_L}\,\mathbf{c}_K\mathbf{c}_L{}^{\dagger} \tag{A 6}$$

as given in (2.10). An exactly similar procedure, applied to the second-order equation, yields (2.15) and (2.16).

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2.4 Teoría Respuesta y Hartree-Fock Acoplado

En las secciones 2.1 y 2.2 se han obtenido las expresiones de las distintas propiedades magnéticas estudiadas en esta tesis, aplicando la Teoría de Perturbaciones de Rayleigh-Schrödinger (TPRS). Sin embargo hay que tener en cuenta que formalmente, en el desarrollo perturbativo dado por esta teoría, se supone conocida la solución exacta del hamiltoniano a orden cero, Ec. (1.14). En la práctica nunca se conoce el estado fundamental exacto a orden cero y siempre se trabaja con aproximaciones al estado fundamental, por ejemplo, Hartree-Fock y DFT por mencionar solamente las aproximaciones con las que se trabaja en esta tesis.
En la bibliografía han sido desarrollados distintos métodos para calcular las *funciones respuesta lineal, cuadrática* y *cúbica* (definidas en la sección 1.3) dependiendo de cuál sea la aproximación utilizada para representar el estado fundamental a orden cero. Así, por mencionar sólo algunos ejemplos, en la ref[48] puede verse el desarrollo teórico de la Teoría Respuesta a nivel MCSCF[e] y en la ref[51] puede observarse el desarrollo de la Teoría Respuesta a nivel DFT.

En la siguiente sección se presenta uno de los posibles desarrollos matemáticos de la Teoría Respuesta al nivel Hartree-Fock, también denominada Hartree-Fock Acoplado (CHF, *Coupled Hartree-Fock*). Se presenta este desarrollo en particular porque es el que ha sido empleado en las implementaciones computacionales de la hipersusceptibilidad magnética, $\mathrm{X}_{\alpha\beta\gamma\delta}$, y la densidad perturbada a segundo orden, $\rho^{B_\alpha B_\beta}(\mathbf{r})$, desarrolladas en el contexto de este trabajo de tesis. (Véase sección 4.1)

2.4.1 Hartree-Fock Acoplado.

A continuación se presenta en forma resumida el método de Hartree-Fock Acoplado en la forma desarrollada por Mc Weeny[52,50]. En esta sección se supone conocido el método de Hartree-Fock para capa cerrada y sólo se hace

[e] A partir de la cual, la Teoría Respuesta a nivel Hartree-Fock puede obtenerse como un caso particular.

un resumen de las principales expresiones para establecer la notación a emplear.

Dado un cierto hamiltoniano (por ejemplo el de la Ec. (2.1)), mediante el método de Hartree-Fock se obtiene como aproximación al estado fundamental una función de onda unideterminantal de la forma:

$$\left|\Psi_{HF}\right\rangle = \left|\phi_1, \bar{\phi}_1, \phi_2, \bar{\phi}_2, \ldots, \phi_{n/2}, \bar{\phi}_{n/2}\right\rangle \qquad (2.36)$$

constituida por los *n/2* orbitales moleculares ϕ_i (doblemente ocupados) de energía orbital más baja, todos ellos son soluciones autoconsistentes de la ecuación de Fock. Los orbitales moleculares ϕ_i se expresan en función de una dada base de *m* orbitales atómicos φ_j (predeterminados antes de iniciar el cálculo de Hartree-Fock)

$$\phi_i = \sum_{j=1}^{m} c_{ij}\varphi_j \qquad (2.37)$$

En general, la base de orbitales atómicos no es ortogonal, por lo cual se define la matriz **S** de solapamiento (overlap) como:

$$S_{ij} = \left\langle \varphi_i \middle| \varphi_j \right\rangle \qquad (2.38)$$

Por otra parte, se puede definir la matriz **R** como[f]:

$$R_{ij} = \sum_{a(ocu)} c_{ai}^{*} c_{aj} \qquad (2.39)$$

donde, si se define el vector columna de *m* elementos:

$$\mathbf{c}_a = \begin{pmatrix} c_{a1} \\ \vdots \\ c_{am} \end{pmatrix} \qquad (2.40)$$

la matriz **R** puede escribirse alternativamente como:

$$\mathbf{R} = \sum_{a(ocu)} \mathbf{c}_a \cdot \mathbf{c}_a^{\dagger} \qquad (2.41)$$

Además, usando que los orbitales moleculares son ortonormales se puede obtener la relación de idempotencia:

[f] A menos de un factor 2, esta matriz es conocida usualmente en la bibliografía como *matriz de cargas y órdenes de enlace*.

$$\mathbf{RSR} = \mathbf{R} \qquad (2.42)$$

Por otro lado, cabe recordar que el operador de Fock es:

$$\hat{f} = \hat{h} + \sum_{a(ocup)} 2\hat{J}_a - \hat{K}_a \qquad (2.43)$$

donde $\hat{h}$ es el operador que involucra a la energía cinética del electrón y a la interacción del electrón con los núcleos y los campos externos. $\hat{J}_a$ y $\hat{K}_a$ son los operadores de Coulomb y de intercambio.

Definiendo la matriz de Fock **f** a partir de los elementos de matriz del operador de Fock en la base atómica ($f_{ij} = \langle \varphi_i | \hat{f} | \varphi_j \rangle$) y en forma análoga la matriz **h** como $h_{ij} = \langle \varphi_i | \hat{h} | \varphi_j \rangle$, se obtiene:

$$\mathbf{f} = \mathbf{h} + \mathbf{G}(\mathbf{R}) \qquad (2.44)$$

con

$$G_{\mathrm{ij}}(\mathbf{R}) = R_{mn}\left(2\langle im | jn \rangle - \langle im | nj \rangle\right) \qquad (2.45)$$

donde las $\langle ij | kl \rangle$ son las integrales bielectrónicas.

Ahora bien, en este método, se propone un desarrollo perturbativo para el operador $\hat{h}$ de manera de considerar a los términos que dependen de los campos externos como “correcciones perturbativas” al término en ausencia de campos $\hat{h}^{(0)}$ de manera que:

$$\mathbf{h} = \mathbf{h}^{(0)} + \mathbf{h}^{(1)} + \mathbf{h}^{(2)} \qquad (2.46)$$

Si bien podría proponerse una serie infinita (como se hace en la ref[52]), para calcular propiedades magnéticas basta con perturbaciones hasta segundo orden en el operador $\hat{h}$.

De manera similar, se propone que las matrices **R** y **f** también se desarrollan perturbativamente de la forma:

$$\mathbf{R} = \mathbf{R}^{(0)} + \mathbf{R}^{(1)} + \mathbf{R}^{(2)} + \ldots \qquad (2.47)$$

$$\mathbf{f} = \mathbf{f}^{(0)} + \mathbf{f}^{(1)} + \mathbf{f}^{(2)} + \ldots \qquad (2.48)$$

donde $\mathbf{f}^{(k)} = \mathbf{h}^{(k)} + G(\mathbf{R}^{(k)})$.

En estos desarrollos se supone resuelto el problema de Hartree-Fock en ausencia de campos, es decir que las matrices sin perturbar $\mathbf{f}^{(0)}$ y $\mathbf{R}^{(0)}$ son conocidas.

Cabe destacar que los desarrollos de las Ec. (2.47) y (2.48) son infinitos a pesar de que el desarrollo para la matriz **h** tenga un número finito de términos.

Claramente la Ec. (2.42) impone restricciones a las matrices $\mathbf{R}^{(1)}$, $\mathbf{R}^{(2)}$,… que pueden ser expresadas convenientemente en función de las "proyecciones" de estas matrices con respecto al subespacio generado por los orbitales ocupados y al generado por los vacantes (en ambos casos se hace referencia a los orbitales sin perturbar).

Para escribir dichos proyectores en forma más clara conviene trabajar con una base atómica ortonormalizada. Recordemos que aplicando, por ejemplo, la ortonormalización simétrica de Löwdin:

$$\tilde{\varphi}_i = \sum_{k=1}^{m} \left(\mathbf{S}^{-1/2} \right)_{ki} \varphi_k \qquad (2.49)$$

se obtiene una base atómica $\tilde{\varphi}_i$ ortonormal. La ventaja de utilizar este tipo de base atómica se observa, por ejemplo, al reescribir la Ec. (2.42) en la nueva base:

$$\tilde{\mathbf{R}}^2 = \tilde{\mathbf{R}} \qquad (2.50)$$

es decir que en este caso la matriz $\tilde{\mathbf{R}}$ es un proyector. Por otro lado, las ecuaciones de Hartree-Fock pueden escribirse de la forma:

$$\tilde{\mathbf{f}}\,\tilde{\mathbf{R}} - \tilde{\mathbf{R}}\,\tilde{\mathbf{f}} = 0 \qquad (2.51)$$

donde $\tilde{f}_{ij} = \langle \tilde{\varphi}_i | \hat{f} | \tilde{\varphi}_j \rangle$.

El proyector sobre los orbitales ocupados sin perturbar está dado por $\tilde{\mathbf{R}}_1 = \tilde{\mathbf{R}}^{(0)}$ y el proyector sobre los orbitales vacantes sin perturbar es: $\tilde{\mathbf{R}}_2 = 1 - \tilde{\mathbf{R}}^{(0)}$ [g]. Estos proyectores permiten descomponer una matriz genérica en sus distintas proyecciones:

$$\begin{aligned} \tilde{\mathbf{A}} &= \tilde{\mathbf{R}}_1 \tilde{\mathbf{A}} \tilde{\mathbf{R}}_1 + \tilde{\mathbf{R}}_1 \tilde{\mathbf{A}} \tilde{\mathbf{R}}_2 + \tilde{\mathbf{R}}_2 \tilde{\mathbf{A}} \tilde{\mathbf{R}}_1 + \tilde{\mathbf{R}}_2 \tilde{\mathbf{A}} \tilde{\mathbf{R}}_2 \\ &= \tilde{\mathbf{A}}_{11} + \tilde{\mathbf{A}}_{12} + \tilde{\mathbf{A}}_{21} + \tilde{\mathbf{A}}_{22} \end{aligned} \qquad (2.52)$$

[g] Recordar que la matriz $\tilde{\mathbf{R}}^{(0)}$ también cumple la Ec. (2.50).

Utilizando en forma combinada las Ec. (2.50) y (2.51) (introduciendo en dichas expresiones los desarrollos perturbativos de $\tilde{\mathbf{R}}$ y $\tilde{\mathbf{f}}$ dados por las Ec. (2.47) y (2.48)), y aplicando convenientemente los proyectores $\tilde{\mathbf{R}}_1$ y $\tilde{\mathbf{R}}_2$, se obtienen las ecuaciones que permiten calcular las distintas proyecciones de las matrices $\tilde{\mathbf{R}}^{(k)}$, es decir: $\tilde{\mathbf{R}}_{11}^{(k)}$, $\tilde{\mathbf{R}}_{12}^{(k)}$, $\tilde{\mathbf{R}}_{21}^{(k)}$ $(=\tilde{\mathbf{R}}_{12}^{(k)\dagger})$ y $\tilde{\mathbf{R}}_{22}^{(k)}$.

En concreto (utilizando nuevamente la base no ortogonal), se puede ver que:

$$\mathbf{R}^{(1)} = \mathbf{x} + \mathbf{x}^{\dagger} \qquad (2.53)$$

donde la matriz $\mathbf{x}\,(=\mathbf{R}_{12}^{(1)})$ cumple la siguiente relación:

$$\mathbf{x} = \sum_{\substack{a(ocu)\\ j(vir)}} \frac{\mathbf{c}_a^{(0)\dagger}\mathbf{f}^{(1)}\mathbf{c}_j^{(0)}}{\varepsilon_a^{(0)} - \varepsilon_j^{(0)}}\mathbf{c}_a^{(0)}\mathbf{c}_j^{(0)\dagger} \qquad (2.54)$$

donde $\mathbf{c}_a^{(0)}$ y $\varepsilon_a^{(0)}$ son, respectivamente, el a-ésimo autovector y su correspondiente autovalor (energía orbital) de la matriz de Fock sin perturbar $\mathbf{f}^{(0)}$.

Dado que la matriz $\mathbf{f}^{(1)}$ depende de la matriz $\mathbf{x}$ $(\mathbf{f}^{(1)} = \mathbf{h}^{(1)} + \mathbf{G}(\mathbf{x}+\mathbf{x}^{\dagger}))$ la ecuación anterior debe ser resuelta iterativamente buscando una solución autoconsistente.

La matriz $\mathbf{R}^{(2)}$ toma la forma:

$$\mathbf{R}^{(2)} = \mathbf{R}_{11}^{(2)} + \mathbf{R}_{12}^{(2)} + \mathbf{R}_{21}^{(2)} + \mathbf{R}_{22}^{(2)} = -\mathbf{x}\mathbf{S}\mathbf{x}^{\dagger} + \mathbf{y} + \mathbf{y}^{\dagger} + \mathbf{x}^{\dagger}\mathbf{S}\mathbf{x} \qquad (2.55)$$

donde sólo queda por determinar la matriz $\mathbf{y}\,(=\mathbf{R}_{12}^{(2)})$. Se puede probar que la matriz **y** cumple la siguiente relación:

$$\mathbf{y} = \sum_{\substack{a(ocu)\\ j(vir)}} \frac{\mathbf{c}_a^{(0)\dagger}\left[\mathbf{f}^{(2)} + \mathbf{S}\cdot\mathbf{x}\cdot\mathbf{f}^{(1)} - \mathbf{x}\cdot\mathbf{f}^{(1)}\cdot\mathbf{S}\right]\mathbf{c}_j^{(0)}}{\varepsilon_a^{(0)} - \varepsilon_j^{(0)}}\mathbf{c}_a^{(0)}\mathbf{c}_j^{(0)\dagger} \qquad (2.56)$$

Como $\mathbf{f}^{(2)}$ depende de la matriz **y** (a través de su dependencia con $\mathbf{R}^{(2)}$), entonces esta matriz también debe calcularse en forma autoconsistente mediante un procedimiento iterativo. Cabe aclarar que a los efectos del cálculo autoconsistente de la Ec. (2.56) , las matrices $\mathbf{f}^{(1)}$ y **x** se suponen conocidas porque lógicamente la Ec. (2.54) debe ser resuelta previamente.

En forma análoga a lo analizado para el primer y segundo orden, para cada orden *k*, la proyección $\mathbf{R}_{12}^{(k)}$ se determina resolviendo una ecuación

autoconsistente similar a las Ec. (2.54) y (2.56) [h]. Mientras que las proyecciones $\mathbf{R}_{11}^{(k)}$ y $\mathbf{R}_{22}^{(k)}$ quedan determinadas por matrices obtenidas en los cálculos de los órdenes anteriores.

De esta manera, las matrices $\mathbf{R}_{11}^{(3)}$ y $\mathbf{R}_{22}^{(3)}$ están dadas por:

$$\mathbf{R}_{11}^{(3)} = -\left(\mathbf{x}\mathbf{S}\mathbf{y}^{\dagger} + \mathbf{y}\mathbf{S}\mathbf{x}^{\dagger}\right) \qquad (2.57)$$

$$\mathbf{R}_{22}^{(3)} = \mathbf{x}^{\dagger}\mathbf{S}\mathbf{y} + \mathbf{y}^{\dagger}\mathbf{S}\mathbf{x} \qquad (2.58)$$

A partir de las expresiones anteriores, ya se dispone de todos los elementos para escribir los desarrollos perturbativos de la energía de Hartree-Fock hasta el cuarto orden. Recordando que la energía de Hartree-Fock está dada por:

$$W = 2\mathrm{Tr}\left[\left(\mathbf{h} + \tfrac{1}{2}\mathbf{G}(\mathbf{R})\right)\cdot\mathbf{R}\right] \qquad (2.59)$$

entonces, aplicando los desarrollos de **h** y **R**, y separando orden a orden, se obtienen los distintos términos perturbativos en la energía $W^{(k)}$:

$$W^{(1)} = 2\mathrm{Tr}\left[\mathbf{h}^{(1)}\cdot\mathbf{R}^{(0)}\right] \qquad (2.60)$$

$$W^{(2)} = 2\mathrm{Tr}\left[\mathbf{h}^{(2)}\cdot\mathbf{R}^{(0)} + \tfrac{1}{2}\mathbf{h}^{(1)}\cdot\mathbf{R}^{(1)}\right] \qquad (2.61)$$

$$W^{(3)} = 2\mathrm{Tr}\left[\mathbf{h}^{(2)}\cdot\mathbf{R}^{(1)} + \mathbf{f}^{(1)}\cdot\left(\mathbf{R}_{11}^{(2)} + \mathbf{R}_{22}^{(2)}\right)\right] \qquad (2.62)$$

$$\begin{aligned} W^{(4)} = 2\mathrm{Tr}\Big[&\tfrac{1}{2}\mathbf{h}^{(2)}\cdot\mathbf{R}^{(2)} + \tfrac{1}{2}\mathbf{f}^{(2)}\cdot\left(\mathbf{R}_{11}^{(2)} + \mathbf{R}_{22}^{(2)}\right) + \tfrac{1}{2}\mathbf{f}^{(1)}\cdot\left(\mathbf{R}_{11}^{(3)} + \mathbf{R}_{22}^{(3)}\right) \\ &+ \mathbf{f}^{(0)}\cdot\left(-\mathbf{R}_{11}^{(2)}\cdot\mathbf{S}\cdot\mathbf{R}_{11}^{(2)} + \mathbf{R}_{22}^{(2)}\cdot\mathbf{S}\cdot\mathbf{R}_{22}^{(2)}\right)\Big] \end{aligned} \qquad (2.63)$$

Cabe destacar que, como es usual en Teoría de Perturbaciones, el cálculo de la corrección en la función de onda hasta un orden *k* (efectuado en este caso a través de la obtención de la matriz $\mathbf{R}^{(k)}$), determina la corrección a la energía hasta el orden 2*k*+1.

[h] Recordar que $\mathbf{R}_{21}^{(k)\dagger} = \mathbf{R}_{12}^{(k)}$

2.4.1.1 Hipersusceptibilidad magnética.

Para efectuar el cálculo del tensor hipersusceptibilidad magnética $X_{\alpha\beta\gamma\delta}$ mediante el método descripto en la sección anterior, debe tomarse como parámetro perturbativo el campo magnético externo **B** (ver sección 2.2).
Para referencias futuras se reescriben las Ec. (2.46) a (2.48) expresando explícitamente la dependencia de esas matrices con el campo magnético:

$$\mathbf{h}(\mathbf{B}) = \mathbf{h}^{(0)} + \mathbf{h}^{B_\alpha} B_\alpha + \mathbf{h}^{B_\alpha B_\beta} B_\alpha B_\beta \qquad (2.64)$$

$$\mathbf{R}(\mathbf{B}) = \mathbf{R}^{(0)} + \mathbf{R}^{B_\alpha} B_\alpha + \mathbf{R}^{B_\alpha B_\beta} B_\alpha B_\beta + \ldots \qquad (2.65)$$

$$\mathbf{f}(\mathbf{B}) = \mathbf{f}^{(0)} + \mathbf{f}^{B_\alpha} B_\alpha + \mathbf{f}^{B_\alpha B_\beta} B_\alpha B_\beta + \ldots \qquad (2.66)$$

Como ya se ha mencionado el operador de Fock $\mathbf{f}^{(0)}$ es el asociado a la molécula aislada en ausencia de campos, descripta mediante el hamiltoniano (1.14).
Los operadores que representan la interacción del electrón con el campo **B** externo, son:

$$\hat{h}^{B_\alpha} = -\frac{1}{2}\hat{l} \qquad (2.67)$$

$$\hat{h}^{B_\alpha B_\beta} = \frac{1}{8}\left(\hat{r}_\gamma \hat{r}_\gamma \delta_{\alpha\beta} - \hat{r}_\alpha \hat{r}_\beta\right) \qquad (2.68)$$

donde se utiliza la notación definida previamente. Cabe recordar que los operadores $\hat{h}^{B_\alpha}$ y $\hat{h}^{B_\alpha B_\beta}$, que actúan en el espacio de un electrón, están relacionados con los operadores $\hat{H}^{B_\alpha}$ y $\hat{H}^{B_\alpha B_\beta}$ definidos en las Ec. (2.9) y (2.10) mediante las expresiones $\hat{H}^{B_\alpha} = \sum_{i=1}^{n} \hat{h}_i^{B_\alpha}$, $\hat{H}^{B_\alpha B_\beta} = \sum_{i=1}^{n} \hat{h}_i^{B_\alpha B_\beta}$.

Si se toma una base atómica compuesta por funciones reales $\varphi_i(\mathbf{r})$ [i], la matriz $\mathbf{h}^{B_\alpha}$ (dada por $h_{ij}^{B_\alpha} = \langle \varphi_i | \hat{h}^{B_\alpha} | \varphi_j \rangle$) es imaginaria pura[j] y antisimétrica. Es sencillo observar, mediante la Ec. (2.54), que las matrices $\mathbf{R}^{B_\alpha}$ y $\mathbf{f}^{B_\alpha}$ también lo son. En

[i] Como es usual, todos los cálculos numéricos de esta tesis han sido efectuados usando bases atómicas de orbitales reales.
[j] Recordar que son matrices hermíticas.

cambio, puede verse que las matrices $\mathbf{h}^{B_\alpha B_\beta}$, $\mathbf{R}^{B_\alpha B_\beta}$ y $\mathbf{f}^{B_\alpha B_\beta}$ son las tres reales y simétricas.

La expresión para las componentes $\mathrm{X}_{\alpha\beta\gamma\delta}$ del tensor hipersusceptibilidad magnética en función de las matrices: $\mathbf{h}^{B_\alpha}$, $\mathbf{R}^{B_\alpha}$, $\mathbf{f}^{B_\alpha}$, etc, puede obtenerse fácilmente a partir de la expresión de $W^{(4)}$, dada por la Ec. (2.63), derivándola 4 veces respecto del campo **B** (tal como indica la Ec. (1.4)).