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Convergence of the Rayleigh–Ritz Method in Self-Consistent-Field and Multiconfiguration Self-Consistent-Field Calculations

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We investigate the analytical convergence of SCF and MCSCF calculations, when the dimension of the subspaces to which the orbitals are restricted tends to infinity. We show that the completeness only in $L^2(R^3; C^2)$ of the orbital bases does not ensure the convergence of the Ritz-energy, neither in SCF nor in MCSCF calculations, but that this convergence – as well as the convergence of the Ritz-orbitals in SCF calculations – is on the contrary guaranteed if the orbital bases are complete in the Sobolev space $W^{1,2}(R^3; C^2)$. Some consequences on the choice of the orbital exponents of Slater and Gauss functions are also discussed.

Key words: Convergence of the Rayleigh–Ritz method – SCF and MCSCF calculations – Completeness of orbital bases.

1. Introduction

During the past fifteen years, calculations of atomic and molecular structure have had a great development and brought relevant contributions to quantum-chemistry. Most of such calculations are variational and are carried out, as it is well known [1, 2], following three general procedures:

(A) Configuration Interaction (CI) *Method*

The electronic wave function Ψ_e is written as $\sum_{I=1}^{L} c^I \Psi^I$, where Ψ^I are fixed Slater determinants (SD) and c^I complex coefficients to be determined to minimize the energy functional[1]

$$E(\Psi_e)=\frac{\langle\Psi_e|H\Psi_e\rangle}{|\Psi_e|^2}.$$

In this equation, the operator

$$H=\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\Delta_i-\sum_{a=1}^{K}\frac{e^2Z_a}{r_{ia}}\right)+\sum_{i<j}\frac{e^2}{r_{ij}}$$

is the Born–Oppenheimer Hamiltonian for N electrons and K nuclei[2], where Z_a is the charge of nucleus a, $r_{ia}\equiv|\boldsymbol{r}_i-\boldsymbol{R}_a|$ and $r_{ij}\equiv|\boldsymbol{r}_i-\boldsymbol{r}_j|$ ($\boldsymbol{r}_i$ and $\boldsymbol{R}_a$ being position operators of electron i and nucleus a, respectively).

(*B*) *Self-Consistent-Field* (SCF) *Method*

Ψ_e is written as a single SD, $\Psi=(1/N!)^{1/2}\det\{\psi^1,\dots,\psi^N\}$, where the one-particle wave functions (orbitals) ψ^i are determined to minimize $E(\Psi_e)$.

(*C*) *Multiconfiguration Self-Consistent-Field* (MCSCF) *Method*

Ψ_e is written as in (A), but in this case both the complex numbers c^I and the orbitals ψ^i, used to construct the SD's Ψ^I, are determined to minimize $E(\Psi_e)$.

These methods, however, have not completely been studied from a rigorous mathematical point of view. Such a study, in our opinion, matters not only because it provides the necessary mathematical foundation, but also because it allows the utilization of some results of the minimization theory [3, 4] and of the approximation theory in Banach spaces [3, 5], which could improve precision and reliability of calculations. We think that the main problems which should be studied to reach this aim are the following:

(1) Existence of the global minimum of the functional $E(\Psi_e)$ on each set considered[3] in (A)–(C).
(2) Convergence[4] of the numerical methods used for the approximate determination of this minimum.
(3) Estimate for the error of the approximations.

In the CI method to our knowledge, the problems (1) and (2) have been solved, but not (3). By this method in fact, approximated eigenvalues and eigenvectors of H are determined. Therefore the minimum existence problem in question is equivalent (cf. [6] p. 6) to the existence problem for the discrete spectrum of H, which, as it is well known has been already solved [7]. The numerical method

[1] From now on we shall denote by $\langle\cdot|\cdot\rangle$ and $|\cdot|$ the usual scalar product and norm of each space L^2 considered in this paper.
[2] Of course, the atomic Hamiltonian is obtained for $K=1$.
[3] That is to say: existence of a wavefunction Ψ_e^*, belonging to the set in question, such that $E(\Psi_e^*)\le E(\Psi_e)$ for all Ψ_e of the set.
[4] In this paper by *convergence* we mean *analytical convergence* and we shall not be concerned with the related numerical problems.

used is that of Rayleigh–Ritz and its convergence properties have been studied, from thirty years ago [8] up to now [9–12].

In the case of SCF method the minimum problem is the one of $E(\Psi_e)$ on the set S of SD's, and the related existence problem has been solved recently [13]. The numerical procedure more widely used[5] consists in writing the orbitals ψ^i as $\sum_{n=1}^{m} c_n^i \phi_n^i$, where the functions ϕ_n^i belong to some complete sets[6] $\{\phi_n^i\}_{n=1}^{\infty}$, $i=1,\ldots,N$, (orbital bases) and then in determining the Nm coefficients c_n^i to minimize $E(\Psi_e)$. To reach this aim, usually the matrix form of the Hartree–Fock equations (cf [1, 2]) is solved, or direct minimization methods for $E(\Psi_e)$ [1, 14] – or also other numerical methods [15] – are used. Anyway, since (whatever is the numerical method adopted) an approximate minimization of $E(\Psi_e)$ is eventually performed by restricting the orbitals to m-dimensional subspaces, the above procedure is nothing but the Rayleigh – Ritz method (RRM) applied to the minimization of $E(\Psi_e)$ on S, as it will be specified better in Sect. 2. In account of this, we shall denote such numerical procedure by SCF-RRM. The *Ritz-energy*, as well as the *Ritz-orbitals*[7] depend on the dimension m of subspaces. Therefore it arises the problem of the convergence of these quantities to the infimum of $E(\Psi_e)$ on S and to the orbitals minimizing exactly $E(\Psi_e)$ on S, respectively, when $m\to\infty$. This convergence, to our knowledge, has not been yet rigorously proved and is generally assumed (cf. [1] p. 116, [2] p. 6, [16] p. 1498, [17] p. 3787 and [18] p. 3958).

Concerning the problem of the estimate of the truncation error, which is of great practical interest in order to estimate rigorously the Hartree–Fock limit, we have a similar situation, since up to now this problem has not been faced in a rigorous mathematical way, but only within a somewhat empirical framework [18].

In the case of MCSCF method, the minimum problem is to minimize $E(\Psi_e)$ on the subset of $S_1\times\cdots\times S_L\times C_1\times\cdots\times C_L$ (where C is the complex field and $\times$ denotes the Cartesian product of sets) described by the linearly independent SD's $\{\Psi^1,\ldots,\Psi^L\}$. As far as we know, the related existence problem has not been solved yet. The numerical procedure used is again the RRM as it was described in the SCF method. Therefore we shall denote such procedure in this case by MCSCF-RRM. Hitherto, neither the convergence properties nor the error estimate in the MCSCF-RRM have been studied. Out of the foregoing unsolved problems we shall consider in this paper only the convergence of the SCF-RRM and of MCSCF-RRM; the remaining problems will be considered in forthcoming papers.

We shall call, according to [9], the convergence of the Ritz-energy to the infimum of $E(\Psi_e)$ and the convergence of the Ritz-orbitals to those ones minimizing

[5] For atoms, however, the numerical integration of the Hartree–Fock equation is often used.
[6] Here we consider in general different orbital bases for different orbitals. However for molecules, we confine ourselves to consider one-centre orbital bases, since all results of this paper deduced in this case remain valid, as we shall see in Sect. 4, also in the case of many-centre orbital bases.
[7] By *Ritz-energy* and *Ritz-orbitals* we mean the value of the minimum of $E(\Psi_e)$ and the corresponding minimizing orbitals, respectively, when the orbital bases are truncated at a finite value m.

$E(\Psi_e)$, when $m \to \infty$, E-convergence and ψ- convergence, respectively. In this paper, for reasons which we shall show in the next section, we take into account the spin without restrictions, and thus our orbitals ψ^i are always supposed to be spinorial functions, namely pairs $\{\psi_+^i, \psi_-^i\}$ where ψ_+^i, ψ_-^i are complex-valued square-integrable functions. The corresponding Hilbert space will be denoted as in [13] by[8] $L_i^2(R^3; C^2)$ (R indicates the real numbers and C the complex ones).

In this work we shall prove that the completeness only in the space $L_i^2(R^3; C^2)$ of the orbital bases $\{\phi_n^i\}_{n=1}^{\infty}$, $i=1,\ldots,N$, is not sufficient to guarantee the E-convergence, neither in the SCF-RRM nor in the MCSCF-RRM, but that the E-convergence is on the contrary ensured in both cases if the sets $\{\phi_n^i\}_{n=1}^{\infty}$ are complete in the Sobolev spaces[9] $W_i^{1,2}(R^3; C^2)$. More precisely we shall show that our more restrictive completeness condition guarantees, in the SCF-RRM, both the E-convergence and the ψ- convergence (in the norm of $L_i^2(R^3; C^2)$). In the MCSCF–RRM, since the problem of the existence of a global minimum of $E(\Psi_e)$ on the subset of $S_1\times\cdots\times S_L\times C_1\times\cdots\times C_L$ previously specified has not yet been solved, we can show only that the completeness in the space $W_i^{1,2}(R^3; C^2)$ of the orbital bases guarantees the $\tilde{E}$-convergence. Our sufficient condition of convergence corresponds exactly to that one of the RRM in the CI method in the form given in [9–11], and implies just the same conditions on the choice of the orbital exponents of Slater and Gauss basis functions in order to ensure the foregoing E-convergence and ψ-convergence. However the procedure for determining it as well as our proof of E-convergence and ψ-convergence, are completely different from those of the CI case, because (although in both cases it is a matter of convergence of the RRM) the two convergences are actually very different. In fact the convergence problem of the RRM in the CI method is equivalent to the convergence problem of the RRM in an eigenvalue equation (Schrödinger equation), while our convergence problem is equivalent to the convergence problem of the RRM in pseudo-eigenvalue equations (Hartree–Fock equations in the SCF–RRM and Fock-like Eqs. [20] in the MCSCF-RRM).

Our results concerning the E-convergence, both of the SCF-RRM and of the MCSCF-RRM, will be obtained in Sect. 2 in the framework of the minimization theory. The ψ-convergence of the SCF-RRM will be proved in Sect 3, by using some results of [13]. In Sect. 4 we shall discuss some implications of our results in current calculations.

2. E-Convergence of the SCF-RRM and of the MCSCF-RRM

For the sake of clearness and simplicity, we firstly consider the problem of the E-convergence of the SCF-RRM, and we start on this section by introducing mathematical preliminaries and notations relevant to this problem only. In the

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[8] Obviously the norm and the scalar product in $L_i^2(R^3; C^2)$ are given by $|\psi^i| = (|\psi_+^i|^2 + |\psi_-^i|^2)^{1/2}$ and $\langle\phi^i|\psi^i\rangle = \langle\phi_+^i|\psi_+^i\rangle + \langle\phi_-^i|\psi_-^i\rangle$, respectively.

[9] $W_i^{1,2}(R^3; C^2)$ denotes the set of pairs $\{\psi_+^i, \psi_-^i\}$ with ψ_+^i, ψ_-^i belonging to the usual Sobolev space (cf. [19] p. 44) $W_i^{1,2}(R^3)$. It is easily seen (by the same arguments as in footnote 17) that completeness in $W_i^{1,2}(R^3: C^2)$ implies completeness in $L_i^2(R^3; C^2)$ but the converse is not true.

final part of this section we shall show that the problem of E-convergence of the MCSCF-RRM is immediately solved as an easy generalization of the SCF-RRM case. In Ref. [13] it was shown that, in general, the energy functional achieves a global minimum on the set of SD's if the orbitals are spinorial functions, and not if, as in practical applications, they are restricted to being products of spatial and spin functions. On the latter more restrictive class of orbitals, there exists a minimum but it is not known whether it is a global minimum or merely a local minimum. For this reason we have supposed here that the orbitals ψ^i are in general pairs $\{\psi^i_+, \psi^i_-\}$, $\psi^i_+, \psi^i_- \in L_i^2(R^3)$. The corresponding Hilbert space has been previously denoted by $L_i^2(R^3; C^2)$, however, from now on, for brevity's sake, we shall denote it simply by[10] L_i^2. The whole Hilbert space of N-electron wavefunctions of space and spin will be represented instead as in [13] by $L^2(R^{3N}; C^{2N})$. As we shall see better in Sect. 4, each result concerning the E-convergence and ψ-convergence derived by us for orbitals belonging to L_i^2 will be valid also for orbitals products of space and spin functions. We set briefly, from now on,

$$-\frac{\hbar^2}{2m}\Delta_i \equiv t_i, \qquad -\sum_{a=1}^{K}\frac{e^2 Z_a}{r_{ia}} \equiv v_i \quad \text{and} \quad \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \equiv w_{ij}.$$

Recalling that in the SCF-RRM the electronic wavefunction is approximated by a single SD

$$\Psi = (N!)^{-1/2} \det\{\psi^1, \ldots, \psi^N\},$$

we denote in this case by $E(\psi^1, \ldots, \psi^N)$ the energy functional. Although $E(\psi^1, \ldots, \psi^N)$ is actually a functional in $L^2(R^{3N}; C^{2N})$, it is more convenient to the aim of this paper, to regard it as a functional in the space $\mathsf{L} = L_1^2 \oplus \cdots \oplus L_N^2$ ($\psi^i \in L_i^2$) ($\oplus$ indicates the direct sum of vectorial spaces). In this space the SD's $\Psi = (N!)^{-1/2} \det\{\psi^1, \ldots, \psi^N\} \neq 0$ are represented by the vectors $(\psi^1, \ldots, \psi^N)$ with linearly independent ψ^i, and the domain $D(E)$ of $E(\psi^1, \ldots, \psi^N)$ by the subset of such vectors which belong to $Q_1(t) \oplus \cdots \oplus Q_N^{(t)}$. We recall that $Q(t) = \{\psi : \langle\psi|t\psi\rangle < \infty\}$ is the quadratic form domain of t (cf. [21], p. 277), and that in our case $Q(t) = D(t^{1/2})$ and[11]

$$\langle\psi^i|t\psi^j\rangle = \langle t^{1/2}\psi^i|t^{1/2}\psi^j\rangle \qquad \forall \psi^i, \psi^j \in D(t^{1/2}) \tag{1}$$

(cf. [22] p. 331). Here $t^{1/2}$ is the square root of t and $D(t^{1/2})$ its domain. The uselfulness of regarding $E(\psi^1, \ldots, \psi^N)$ as functional in L lies in identifying easily and rigorously the SCF-RRM as a particular case of the RRM[12]. To reach this aim in fact, it is sufficient to consider L as the Banach space on which the method is applied and to consider as subspace where $E(\psi^1, \ldots, \psi^N)$ is minimized that

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[10] Whenever the orbital index i is not relevant we shall denote the space $L^2(R^3; C^2)$ simply by L^2. The symbol L^2 should not be confused with the symbol of the usual Hilbert space of only spatial orbitals. For the sake of clearness this latter space will be denoted by $L_i^2(R^3)$ or $L^2(R^3)$.

[11] This property, as well as other properties of linear operators in Hilbert space which we shall use, are proved in the space $L^2(R^3)$, but, as it is seen immediately they remain valid in the space L^2.

[12] For a rigorous definition of the RRM, see [3] or [4].

one spanned by m elements of the complete system in[13] L: $\{(\phi_n^1, \ldots, 0) \ldots (0, \ldots, \phi_n^N)\}_{n=1}^{\infty}$. We shall denote by E_∞ and by $(\psi_\infty^1, \ldots, \psi_\infty^N)$ the infimum of $E(\psi^1, \ldots, \psi^N)$ on $D(E)$ and a minimizing vector, respectively, namely:

$$E_\infty \equiv E(\psi_\infty^1, \ldots, \psi_\infty^N) = \inf_{D(E)} E(\psi^1, \ldots, \psi^N). \tag{2}$$

Now we give a sufficiency condition for the E-convergence of the SCF-RRM by means of a theorem [3, 4] of minimization theory concerning the convergence of the RRM in general. For reader's convenience we report this theorem here.

Theorem 1:

(a) Let Q be any set in Banach space X and let $F(x)$ be a continuous functional on Q.
(b) Let $\{\Phi_n\}_{n=1}^{\infty}$ a complete system in X.
(c) Suppose there exists a vector $x_m \in L_m \cap Q$, where L_m is the m-dimensional subspace spanned by $\{\Phi_1, \ldots, \Phi_m\}$, so that $\min_{x \in L_m \cap Q} F(x) = F(x_m) \equiv F_m$.
(d) Suppose that $\inf_{x \in Q} F(x) = F_\infty$ is finite.
Then $\lim_{m \to \infty} F_m = F_\infty$.

In other words this theorem guarantees, so long as (c) and (d) are satisfied, that the sequence of the Rayleigh–Ritz upper bounds F_m converges to the infimum F_∞, if it is used a basis set complete in the norm topology with respect to which the functional in question turns out to be continuous. Now, in our case, (c) and (d) are satisfied, as can be seen easily. However, concerning (a) we have the following

Proposition 1:

The functional $E(\psi^1, \ldots, \psi^N)$ is not continuous in L, namely in the topology of the norm of L

$$|(\psi^1, \ldots, \psi^N)| = (|\psi^1|^2 + \cdots + |\psi^N|^2)^{1/2}, \tag{3}$$

at any $(\psi^1, \ldots, \psi^N) \in D(E)$.

Proof:

Remembering a well known formula (cf. [23] p. 1480) for the matrix elements of an operator with respect to two SD's, we can write

$$E(\psi^1, \ldots, \psi^N) = \frac{\sum_{k,l=1}^{N} \langle \psi^k | (t+v) \psi^l \rangle D[k, l] + \frac{1}{2} \sum_{\substack{pq \\ rs}}^{N} \langle \psi^p \psi^q | w \psi^r \psi^s \rangle D[pq, rs]}{\det \{\langle \psi^i | \psi^j \rangle\}}, \tag{4}$$

[13] We recall that by $\{\phi_n^i\}_{n=1}^{\infty}$, $i = 1, \ldots, N$, we are denoting the basis sets (momentarily supposed complete only in L_i^2) in terms of which the orbitals are expanded.

where $D[k, l]$ is the first rank minor assigned to the k-row and l-column of the matrix $\{\langle\psi^i|\psi^j\rangle\}$, $i, j = 1, 2, \ldots N$, and $D[pq, rs]$ is the second rank minor of the same matrix assigned to the p, q-rows and r, s-columns and antisymmetrized in these indices. Now we consider the sesquilinear form $\langle\psi^k|t\psi^l\rangle$. Owing to the unboundedness of t in L^2, it is not bounded in L and thus two sequences $\{\psi_n^k\}_{n=1}^{\infty}$ and $\{\psi_n^l\}_{n=1}^{\infty}$ exist such that

$$\langle\psi_n^k|t\psi_n^l\rangle = c_n^k c_n^l |\psi_n^k||\psi_n^l| \tag{5}$$

where $c_n^k \to \infty$ and $c_n^l \to \infty$.

By defining, $\forall(\psi_0^1, \ldots, \psi_0^N) \in D(E)$, the new sequences $\{\psi_n'^k\}_{n=1}^{\infty}$ and $\{\psi_n'^l\}_{n=1}^{\infty}$, where

$$\psi_n'^k = \frac{1}{c_n^k}\frac{\psi_n^k}{|\psi_n^k|} + \psi_0^k \quad \text{and} \quad \psi_n'^l = \frac{1}{c_n^l}\frac{\psi_n^l}{|\psi_n^l|} + \psi_0^l,$$

which are strongly convergent in L^2 to ψ_0^k snd ψ_0^l, respectively, we get by (5)

$$\lim_{n\to\infty} \langle\psi_n'^k|t\psi_n'^l\rangle = 1 + \langle\psi_0^k|t\psi_0^l\rangle.$$

Therefore, recalling the well known definition of continuity (cf. [21] p. 6), the sesquilinear form $\langle\psi^k|t\psi^l\rangle$ is not continuous in L at any $(\psi_0^1, \ldots, \psi_0^N) \in D(E)$. Just the same proof can be carried out for the sesquilinear form $\langle\psi^k|v\psi^l\rangle$.

In the case of $\langle\psi^p\psi^q|w\psi^r\psi^s\rangle$ we can fix ψ^q and ψ^r (ψ^p and ψ^s) in order to get, using the same proof as above, that $\langle\psi^p\psi^q|w\psi^r\psi^s\rangle$ is not continuous in L with respect to ψ^p and ψ^s(ψ^q and ψ^r), and hence with respect to ψ^p, ψ^q, ψ^r, ψ^s at any $(\psi_0^1, \ldots, \psi_0^N) \in D(E)$. Thus by taking into account (4), the proposition is proved.

We remark that the hypothesis (a) of Theorem 1 can be weakened (cf. [4]) requiring that $F(x)$ is only semicontinuous from below on Q. However also this weaker condition is not satisfied by $E(\psi^1, \ldots, \psi^N)$. We omit the proof of this statement for the sake of brevity.

As a consequence, we have that the use in the SCF-RRM of orbital bases $\{\phi_n^i\}_{n=1}^{\infty}$ complete only in L_i^2 (or – this is the same – of basis sets $\{(\phi_n^1, \ldots, 0) \cdots (0, \ldots, \phi_n^N)\}_{n=1}^{\infty}$ complete only in L) is not sufficient to ensure the E-convergence.

In order to satisfy the hypothesis (a) of Theorem 1 in our case, we introduce a new topology on L with respect to which $E(\psi^1, \ldots, \psi^N)$ becomes continuous.

Proposition 2:

Set,

$$\forall\psi, \phi \in D(t^{1/2}) \equiv Q(t),$$

$$(\phi|\psi) = \langle\phi|\psi\rangle + \langle t^{1/2}\phi|t^{1/2}\psi\rangle \tag{6}$$

$$\|\psi\|^2 = |\psi|^2 + |t^{1/2}\psi|^2 \tag{7}$$

where (see footnote[8]) $\langle\cdot|\cdot\rangle$ and $|\cdot|$ denote scalar product and norm of L^2, respectively. Then expression (6) defines on $Q(t)$ a new scalar product and $Q(t)$ becomes, in the topology of the new norm (7), the Sobolev space[14] $W^{1,2}(R^3; C^2)$.

Proof:

Since $t^{1/2}$ is a closed operator from L^2 to L^2, the proof of [24] p. 207 holds equally well here. Taking into account footnote[8] and the definition of the space $W^1(R^3)$ (cf. [19] p. 44) we get

$$(\phi|\psi) = (\phi_+|\psi_+) + (\phi_-|\psi_-) \tag{8}$$

and

$$\|\psi\|^2 = \|\psi_+\|^2 + \|\psi_-\|^2, \tag{9}$$

where $(\phi_\pm|\psi_\pm)$ and $\|\psi_\pm\|$ are the scalar product and norm of $W^1(R^3)$, respectively. Thus the proposition is proved.

Proposition 3:

Let us denote by W the space $W_1^1 \oplus, \ldots, \oplus W_N^1(\psi^i \in W_i^1)$, then $E(\psi^1, \ldots, \psi^N)$ is continuous in W, namely continuous in the topology of the norm of W

$$\|(\psi^1, \ldots, \psi^N)\| = (\|\psi^1\|^2 + \cdots + \|\psi^N\|^2)^{1/2}, \tag{10}$$

at any $(\psi^1, \ldots, \psi^N) \in D(E)$.

Proof:

In virtue of expression (4) the proposition will be proved if we shall show the continuity in W of $\langle\psi^k|t\psi^l\rangle$, $\langle\psi^k|v\psi^l\rangle$ and $\langle\psi^p\psi^q|w\psi^r\psi^s\rangle$ since the continuity in W of $D[k, l], D[pq, rs]$ and det $\{\langle\psi^i|\psi^j\rangle\}$ is obvious. Let $\{(\psi_n^1, \ldots, \psi_n^N)\}_{n=1}^\infty$ a sequence belonging to $D(E)$ and strongly convergent in W to $(\psi_0^1, \ldots, \psi_0^N) \in D(E)$, then, as easily can be seen[15], (e) $\psi_n^i \to \psi_0^i$ (f) $t^{1/2}\psi_n^i \to t^{1/2}\psi_0^i$ in L_i^2 and (g) $\psi_n^i\psi_n^j \to \psi_0^i\psi_0^j$ (h) $(t+t)^{1/2}\psi_n^i\psi_n^j \to (t+t)^{1/2}\psi_0^i\psi_0^j$ in $L_i^2 \otimes L_j^2$. By (1) and (f) we get

$$\lim_{n\to\infty} \langle\psi_n^k|t\psi_n^l\rangle = \lim_{n\to\infty} \langle t^{1/2}\psi_n^k|t^{1/2}\psi_n^l\rangle = \langle t^{1/2}\psi_0^k|t^{1/2}\psi_0^l\rangle = \langle\psi_0^k|t\psi_0^l\rangle.$$

By the inequality

$$\langle\psi^k|-v\psi^l\rangle \le (\langle\psi^k|-v\psi^k\rangle)^{1/2}(\langle\psi^l|-v|\psi^l\rangle)^{1/2}$$

(cf. [22] p. 310), by the t-boundedness of $-v$ in the quadratic form

$$\langle\psi|-v\psi\rangle \le a|\psi|^2 + b|t^{1/2}\psi|^2, \qquad a, b > 0, \qquad \forall\psi \in W^1 \tag{11}$$

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14 From now on, we shall denote the space $W^{1,2}(R^3; C^2)$ simply by W^1 and, when the orbital index i is relevant, by W_i^1. The usual Sobolev space of spatial orbitals will be always denoted by $W_i^1(R^3)$ or $W^1(R^3)$.

15 The symbol $\to$ denotes here strong convergence.

(cf. [22] pp. 302, 321), and by (e) and (f), we get

$$\lim_{n\to\infty} |\langle\psi_n^k|v\psi_n^l\rangle - \langle\psi_0^k|v\psi_0^l\rangle|$$
$$= \lim_{n\to\infty} |\langle\psi_n^k - \psi_0^k|v(\psi_n^l - \psi_0^l)\rangle + \langle\psi_n^k - \psi_0^k|v\psi_0^l\rangle + \langle\psi_0^k|v(\psi_n^l - \psi_0^l)\rangle|$$
$$\leq \lim_{n\to\infty} \{(\langle\psi_n^k - \psi_0^k| - v(\psi_n^k - \psi_0^k)\rangle)^{1/2}(\langle\psi_n^l - \psi_0^l| - v(\psi_n^l - \psi_0^l)\rangle)^{1/2}$$
$$+ |\psi_n^k - \psi_0^k|\,|v\psi_0^l| + |v\psi_0^k|\,|\psi_n^l - \psi_0^l|\} = 0.$$

Finally, by the inequality

$$\langle\psi^p\psi^q|w\psi^r\psi^s\rangle \leq (\langle\psi^r\psi^s|w\psi^r\psi^s\rangle)^{1/2}(\langle\psi^p\psi^q|w\psi^p\psi^q\rangle)^{1/2},$$

by the $(t+t)$-boundedness in the quadratic form of w

$$\langle\psi^i\psi^j|w\psi^i\psi^j\rangle \leq a'|\psi^i\psi^j|^2 + b'|(t+t)^{1/2}\psi^i\psi^j|^2, \qquad a', b' > 0 \qquad \forall\psi^i, \psi^j \in W^1$$

(cf. [8] p. 203 and [22] p. 321), and by (g) and (h), we get exactly as above

$$\lim_{n\to\infty} |\langle\psi_n^p\psi_n^q|w\psi_n^r\psi_n^s\rangle - \langle\psi_0^p\psi_0^q|w\psi_0^r\psi_0^s\rangle| = 0.$$

Thus the proposition is proved.

Now the SCF–RRM can be identified as a particular case of the RRM of Theorem 1, by taking as Banach space X the space W, as basis $\{\Phi_n\}_{n=1}^{\infty}$ the set $\{(\phi_n^1, \ldots, 0) \cdots (0, \ldots, \phi_n^N)\}_{n=1}^{\infty}$ which is complete in W if the orbital bases $\{\phi_n^i\}_{n=1}^{\infty}$ are complete in W_i^1, and as subspace L_m the subspace $W_{1m}^1 \oplus \cdots \oplus W_{Nm}^1$, where the W_{im}^1 are the m-dimensional spaces spanned by $\{\phi_1^i, \ldots, \phi_m^i\}$. As the set $\{(\phi_n^1, \ldots, 0) \cdots (0, \ldots \phi_n^N)\}_{n=1}^{\infty}$ is complete in a topology with respect to which, by Proposition 3, the functional $E(\psi^1, \ldots, \psi^N)$ turns out to be continuous, we have, denoting from now on by E_m the Ritz-energy, namely the minimum of $E(\psi^1, \ldots, \psi^N)$ on $D(E) \cap W_{1m}^1 \oplus \cdots \oplus W_{Nm}^1$, the following

Proposition 4:

If in the SCF–RRM one takes as orbital bases, sets $\{\phi_n^i\}_{n=1}^{\infty}$ complete in W_i^1, $i = 1, \ldots, N$, then $\lim_{m\to\infty} E_m = E_\infty$.

Now we consider the E-convergence of the MCSCF–RRM. In this case the N-electron wavefunction is written as $\sum_{I=1}^{L} c^I\psi^I$, where the ψ^I are the L linear independent SD's which can be built by the M orbitals $\{\psi^1, \ldots, \psi^M\}$ $(M > N)$. The energy functional depends, thus, both on the orbitals $\{\psi^1, \ldots, \psi^M\}$ and the complex numbers $\{c^1, \ldots, c^L\}$, and therefore, we shall denote it by $E(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L)$. The MCSCF-RRM differs from the SCF-RRM only formally, and all what we said for the latter can be repeated here, provided that the space L is replaced by the new space $L_1^2 \oplus \cdots \oplus L_M^2 \oplus C_1 \oplus \cdots \oplus C_L$ and the space W by the new space $W_1^1 \oplus \cdots \oplus W_M^1 \oplus C_1 \oplus \cdots \oplus C_L$.

More precisely, we have the following propositions:

Proposition 5:

The functional $E(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L)$ is not continuous in $L_1^2 \oplus \cdots \oplus L_M^2 \oplus C_1 \oplus \cdots \oplus C_L$ at any $(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L)$ belonging to its domain $D(E)$.

Proposition 6:

The functional $E(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L)$ is continuous in $W_1^1 \oplus \cdots \oplus W_M^1 \oplus C_1 \oplus \cdots \oplus C_L$ at any $(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L) \in D(E)$.

We shall not give detailed proof of these propostions because it follows from an easy extension of the proof of Propositions 1, 3. In fact, it is sufficient to replace (4) by the new expression

$$E(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L) = \frac{\sum_{IJ=1}^{L} c^I c^{J*} \left(\sum_{kl} \langle \psi_I^k | (t+v) \psi_J^l \rangle D_{IJ}[k, l] + \sum_{\substack{pq \\ rs}} \langle \psi_I^p \psi_I^q | w \psi_J^r \psi_J^s \rangle D_{IJ}[pq, rs] \right)}{\sum_{IJ=1}^{L} c^I c^{J*} \det \{\langle \psi_I^i | \psi_J^j \rangle\}},$$

which differs from (4) for the summation on the indices I, J of SD's and for the fact that the summation on the orbital indices k, l, ... is restricted to those indices which appear in SD in consideration (the meaning of any other notation remaining the same). Finally, since the minimum of $E(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L)$ on $D(E) \cap W_{1m}^1 \oplus \cdots \oplus W_{Mm}^1 \oplus C_1 \oplus \cdots \oplus C_L$, namely the Ritz-energy E_m, exists – as it can be immediately seen – since the infimum E_∞ of $E(\psi^1, \ldots, \psi^M, c^1, \ldots, c^L)$ on $D(E)$ is finite owing to the boundedness from below of H and since Proposition 6 holds, the hypotheses (a), (c) and (d) of Theorem 1 are satisfied. Thus we get (analogously to the SCF–RRM) the following sufficiency condition for the E-convergence of the MCSCF-RRM.

Proposition 7:

If in the MCSCF–RRM, one takes as orbital bases, sets $\{\phi_n^i\}_{n=1}^\infty$ complete in W_i^1, $i = 1, \ldots, M$, then $\lim_{m\to\infty} E_m = E_\infty$.

3. ψ-Convergence of the SCF-RRM

Concerning the ψ-convergence of the SCF–RRM we have the following

Theorem 2:

(i) Suppose that complete sets in W_i^1 are taken as orbital bases.
Let $(\psi_m^1, \ldots, \psi_m^N)$ be the Ritz-orbitals, namely the vector minimizing $E(\psi^1, \ldots, \psi^N)$ on $D(E) \cap W_{1m}^1 \oplus \cdots \oplus W_{Nm}^1$, and let $\{(\psi_m^1, \ldots, \psi_m^N)\}_{m=m_1,m_2,\cdot}^\infty (m_i > m_j$ if

$i>j$) be the sequence of the Ritz-orbitals obtained by performing successive SCF-RRM calculations.
(ii) Suppose that $\langle\psi^i_m|\psi^j_m\rangle=\delta_{ij}$ at each m.
Then the sequence $\{(\psi^1_m,\ldots,\psi^N_m)\}^\infty_{m=m_1}$ contains a subsequence $\{(\psi^1_{m'},\ldots,\psi^N_{m'})\}^\infty_{m'=m_1'}$ such that

$$\lim_{m'\to\infty}|\psi^i_{m'}-\psi^i_\infty|=0,\qquad i=1,\ldots,N$$

being (see (2)) the ψ^i_∞ orbitals which minimize $E(\psi^1,\ldots,\psi^N)$ on $D(E)$ and $|\cdot|$ (see footnotes 1, 8) the norm of L^2_i.

Proof:

As $\lim_{m\to\infty}E(\psi^1_m,\ldots,\psi^N_m)\equiv\lim_{m\to\infty}E_m=E_\infty$ by Proposition 4 and $E_{m_i}<E_{m_j}$ if $m_i>m_j$, then there exists a dimension m_k of the subspaces such that for any $m>m_k$

$$E_m<E_\infty+1.$$

Writing the explicit expression of E_m in this inequality, we get immediately

$$\sum_{i=1}^N\langle\psi^i_m|t\psi^i_m\rangle\le1+E_\infty-\sum_{i=1}^N\langle\psi^i_m|v\psi^i_m\rangle-\tfrac12\sum_{i,j=1}^N\langle\psi^i_m\psi^j_m|\tilde w\psi^i_m\psi^j_m\rangle,$$

where $\tilde w$ denotes the antisymmetrized w.
This latter inequality, remembering that by (i) $\psi^i_m\in W^1_i$, yields, by (11) (where we take $b<1$), by (ii), by positiveness of w and definition (7)

$$\|\psi^i_m\|^2\le1+\frac{1+E_\infty+Na}{1-b},\qquad\forall\, m>m_k,\qquad i=1,\ldots,N.$$

Hence the sequence $\{(\psi^1_m,\ldots,\psi^N_m)\}^\infty_{m=m_1}$, which is bounded in L by construction, is bounded in W too. Therefore it contains (cf. [22] p. 253) a subsequence $\{(\psi^1_{m'},\ldots,\psi^N_{m'})\}^\infty_{m'=m_1'}$ convergent both in the weak-L topology and in the weak-W topology to a vector[16] $(\psi^1_\infty,\ldots,\psi^N_\infty)\in$ W. In other words $\forall\,(\phi^1,\ldots,\phi^N)\in$ W

$$\lim_{m'\to\infty}(\phi^1,\ldots,\phi^N|\psi^1_{m'},\ldots,{}^N_{m'})=(\phi^1,\ldots,\phi^N|\psi^1_\infty,\ldots,\psi^N_\infty),\tag{12}$$

where $(\cdot,\ldots,\cdot|\cdot,\ldots,\cdot)$ is the scalar product of W, and $\forall(\phi^1,\ldots,\phi^N)\in L$

$$\lim_{m'\to\infty}\langle\phi^1,\ldots,\phi^N|\psi^1_{m'},\ldots,\psi^N_{m'}\rangle=\langle\phi^1,\ldots,\phi^N|\psi^1_\infty,\ldots,\psi^N_\infty\rangle,\tag{13}$$

where $\langle\cdot,\ldots,\cdot|\cdot,\ldots,\cdot\rangle$ is the scalar product of L. Since, as it is obvious, in virtue of (12) the orbitals $\psi^i_{m'}$ converge to ψ^i_∞, $i=1,\ldots,N$, both in the weak-W^1_i

[16] We denote this vector by $(\psi^1_\infty,\ldots,\psi^N_\infty)$ because, as we shall see shortly, it is a minimizing vector.

topology and the weak -L_i^2 topology, it can be proved exactly as in [13] (see also references therein quoted) that

$$\langle\psi^i_\infty|t\psi^i_\infty\rangle \le \liminf_{m'\to\infty} \langle\psi^i_{m'}|t\psi^i_{m'}\rangle$$

$$\langle\psi^i_\infty\psi^j_\infty|\tilde{w}\psi^i_\infty\psi^j_\infty\rangle \le \liminf_{m'\to\infty} \langle\psi^i_{m'}\psi^j_{m'}|\tilde{w}\psi^i_{m'}\psi^j_{m'}\rangle,$$

and

$$\langle\psi^i_\infty|v\psi^i_\infty\rangle = \lim_{m'\to\infty} \langle\psi^i_{m'}|v\psi^i_{m'}\rangle.$$

Thus, remarking that also for the subsequence $\{(\psi^1_{m'},\ldots,\psi^N_{m'})\}_{m'=m_1'}^\infty$ it is

$$\lim_{m'\to\infty} E(\psi^1_{m'},\ldots,\psi^N_{m'}) \equiv \lim_{m'\to\infty} E_{m'} = E_\infty,$$

we get

$$\begin{aligned}\sum_{i=1}^N \langle\psi^i_\infty|(t+v)\psi^i_\infty\rangle + \frac{1}{2}\sum_{i,j=1}^N \langle\psi^i_\infty\psi^j_\infty|\tilde{w}\psi^i_\infty\psi^j_\infty\rangle \\ \le \sum_{i=1}^N \liminf_{m'\to\infty} \langle\psi^i_{m'}|(t+v)\psi^i_{m'}\rangle + \frac{1}{2}\sum_{i,j=1}^N \liminf_{m'\to\infty} \langle\psi^i_{m'}\psi^j_{m'}|\tilde{w}\psi^i_{m'}\psi^j_{m'}\rangle \\ \le \liminf_{m'\to\infty} E(\psi^1_{m'},\ldots,\psi^N_{m'}) = \lim_{m'\to\infty} E(\psi^1_{m'},\ldots,\psi^N_{m'}) = E_\infty. \qquad (14)\end{aligned}$$

Now in [13] there is considered an *extended* energy functional, namely the functional

$$\sum_{i=1}^N \langle\psi^i|(t+v)\psi^i\rangle + \tfrac{1}{2}\sum_{i,j=1}^N \langle\psi^i\psi^j|\tilde{w}\psi^i\psi^j\rangle$$

on the set

$$\mathsf{M} = \{(\psi^1,\ldots,\psi^N): \langle\psi^i|\psi^j\rangle = M_{ij}, \quad 0\le M_{ij}\le 1, \quad i,j=1,\ldots,N\},$$

and it is shown that, in the case of $N<Z+1$ (where $Z=\sum_{a=1}^K Z_a$ is the total nuclear charge), it attains the global minimum at a vector $(\psi^1,\ldots,\psi^N)$ with $\langle\psi^i|\psi^j\rangle=\delta_{ij}$.

As this extended functional agrees with ours when $M_{ij}=\delta_{ij}$, then E_∞ is the minimum not only of our functional $E(\psi^1,\ldots,\psi^N)$ but also of the extended functional. Therefore, because in general $\langle\psi^i_\infty|\psi^j_\infty\rangle = M^\infty_{ij}$ with $0\le M^\infty_{ij}\le 1$, $i,j=1,\ldots,N$, (cf. [13] Lemma 2.2) and hence $(\psi^1_\infty,\ldots,\psi^N_\infty)\in\mathsf{M}$, the relation (14) yields the equation

$$\sum_{i=1}^N \langle\psi^i_\infty|(t+v)\psi^i_\infty\rangle + \tfrac{1}{2}\sum_{i,j=1}^N \langle\psi^i_\infty\psi^j_\infty|\tilde{w}\psi^i_\infty\psi^j_\infty\rangle = E_\infty.$$

Recalling the general expression for E_∞ which can be obtained from (4), we get by the above equation

$$\det\{\langle\psi^i_\infty|\psi^j_\infty\rangle\}=1$$

$$D[k,l]=\begin{cases}0 & \text{if } k\neq l\\ 1 & \text{if } k=l\end{cases}\qquad D[pq,rs]=\begin{cases}0 & \text{if } (pq)\neq(rs)\\ 1 & \text{if } (pq)=(rs).\end{cases}$$

These last equations imply, by well known properties of determinants and matrices, that $\langle\psi^i_\infty|\psi^j_\infty\rangle=\delta_{ij}$ and hence that $(\psi^1_\infty,\ldots,\psi^N_\infty)$ minimizes $E(\psi^1,\ldots,\psi^N)$ on $D(E)$. In other words we have proved that the subsequence $\{(\psi^1_{m'},\ldots,\psi^N_{m'})\}^\infty_{m'=m_1}$ converges weakly, both in W and in L, to a minimizing vector $(\psi^1_\infty,\ldots,\psi^N_\infty)$ of our functional.

We complete the proof of this theorem showing that the subsequence $\{(\psi^1_{m'},\ldots,\psi^N_{m'})\}^\infty_{m'=m_1}$ converges strongly in L to $(\psi^1_\infty,\ldots,\psi^N_\infty)$. By (ii) and by the result proved above $\langle\psi^i_\infty|\psi^j_\infty\rangle=\delta_{ij}$, we have

$$\lim_{m'\to\infty}|(\psi^1_{m'},\ldots,\psi^N_{m'})|=|(\psi^1_\infty,\ldots,\psi^N_\infty)| \tag{15}$$

where $|(\cdot,\ldots,\cdot)|$ (cf. (3)) denotes the norm of L. Now this convergence (15) together with the weak convergence in L (13) imply (cf. [22] p. 253) the strong convergence in L of $\{(\psi^1_{m'},\ldots,\psi^N_{m'})\}^\infty_{m'=m_1}$ to $(\psi^1_\infty,\ldots,\psi^N_\infty)$, i.e.

$$\lim_{m'\to\infty}|(\psi^1_{m'},\ldots,\psi^N_{m'})-(\psi^1_\infty,\ldots,\psi^N_\infty)|=0$$

or, which is the same,

$$\lim_{m'\to\infty}|\psi^i_{m'}-\psi^i_\infty|=0,\qquad i=1,\ldots,N.$$

4. Conclusive Remarks

The requirement of the completeness in W^1 of the orbital bases, in order to ensure the convergence of the SCF–RRM and MCSCF–RRM, corresponds exactly to the co-called *Michlin's criterion* (cf. [9, 11]) of convergence of the RRM in the CI method. In the case of that method, however, there exists a more restrictive sufficient condition of convergence which was firstly derived by Kato [8] and recently reconsidered in [9, 11] (in [9] it has been named *Kato's criterion*). Also in the SCF–RRM and MCSCF–RRM we can immediately derive another sufficient condition of convergence which corresponds exactly to Kato's criterion. To this end, we define $\forall\psi\in D(t)$ the new norm

$$|||\psi|||^2=|\psi|^2+|t\psi|^2.$$

By the same arguments in the proof of Proposition 2, it can easily be seen that $D(t)$ equipped with this new norm becomes the Sobolev space $W^{2,2}(R^3;C^2)$ (i.e. the set of pairs $\{\psi_+,\psi_-\}$ of complex-valued functions, with each function belonging to the ordinary Sobolev space $W^{2,2}(R^3)$). From now on, we shall briefly indicate $W^{2,2}(R^3; C^2)$ by W^2 ($W_i^{2,2}(R^3; C^2)$ by W_i^2) and $W^{2,2}(R^3)$ by $W^2(R^3)$ ($W_i^{2,2}(R^3)$ by $W_i^2(R^3)$). As strong convergence in W^2 implies strong convergence in[17] W^1, we get immediately that Propositions 3, 6 remain valid even if the spaces W_i^1 are replaced by the spaces W_i^2. As a consequence of the continuity of the energy functional in this new topology we can state that the E-convergence of the SCF–RRM and MCSCF–RRM as well as the ψ-convergence of the SCF–RRM are guaranteed provided that one uses orbital bases $\{\phi_n^i\}_{n=1}^\infty$ complete[18] in W_i^2, $i=1, \ldots, N$. Let us remark that both our conditions for E-convergence and ψ-convergence are only sufficient and not necessary. Therefore it is not excluded that E-convergence as well as ψ-convergence can take place, even when orbital bases $\{\phi_n^i\}_{n=1}^\infty$ complete only in L_i^2 are used. Furthermore, with regard to ψ-convergence, as far as we know, no theorem analogous to Theorem 1 exists, which explicitly states that the completeness only in L_i^2 of orbital bases does not guarantee ψ-convergence. Thus, it seems to us that the conditions for ψ-convergence are less restrictive, and it might happen that, by using in the SCF–RRM orbital bases $\{\phi_n\}_{n=1}^\infty$ complete only in L_i^2, the ψ-convergence takes place and E-convergence does not. Anyway, such a situation, although curious, would be explained by the discontinuity everywhere of $E(\psi^1, \ldots, \psi^N)$ in L. In fact, in this case the convergence in L of $(\psi_m^1, \ldots, \psi_m^N)$ to $(\psi_\infty^1, \ldots, \psi_\infty^N)$ does not imply the convergence of E_m to E_∞.

Our sufficient criterion of convergence is valid for arbitrary atoms and molecules, and it requires for the latter the completeness in W_i^1 $i=1, \ldots, N$, of one-centre orbital bases only. If this is the case, the addition of other orbital bases (even if not complete in W_i^1) centered at different sites, does not destroy the convergence, but, on the contrary, increases its speed. Therefore the convergence is always ensured by our criterion in molecular calculations, performed by using many-centre orbital bases (so as in the usual calculations where the bases are centered at the nuclei of the molecule), provided that at least one set of one-centre orbital bases (no matter where it is centered) is complete in W_i^1.

As to the analysis of the completeness properties in the spaces here introduced of the orbital bases mostly used in SCF-RRM and MCSCF–RRM calculations, we refer the reader to the exhaustive study performed by Klahn and Bingel [10]. We remark only that those authors indicated by $H_A(R^3)$ and $H_{A^2}(R^3)$ the Sobolev spaces here denoted by $W^1(R^3)$ and $W^2(R^3)$, respectively, and that they studied completeness property of spatial orbital bases only since the introduction of spin changes nothing (cf. [9] p. 21 and footnote[17] of the present work).

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[17] The imbedding of $W^2(R^3)$ in $W^1(R^3)$ (cf, [19]) implies the imbedding of W^2 in W^1. More generally, any properties involving convergence (as completeness property) which hold for the spaces $W^2(R^3)$ and $W^1(R^3)$ disregarding the spin remain valid for our spaces W^2 and W^1, which take into account the spin. This follows easily from expression (9) for the norm of W^1 and from expression $|||\psi||| = (|||\psi_+|||^2 + |||\psi_-|||^2)^{1/2}$ for the norm of W^2.

[18] Since completeness in W^2 implies completeness in W^1 (see footnote[17]), this latter convergence criterion is included in the former.

In the actual calculations the orbitals, as we said, are generally restricted to being products of space and spin functions. In this case the energy functional depends only on the spatial part of the orbitals. Hence the spaces L_i^2, W_i^1 and W_i^2, which take into account the spin, are replaced by the spaces $L_i^2(R^3)$, $W_i^1(R^3)$ and $W_i^2(R^3)$, which neglect the spin. It is immediately seen that, even with this replacement of spaces, everything said in this work remains valid. In particular we can state that if – in the case of orbitals products of space and spin functions – one takes, as orbital bases, sets $\{\phi_n^i\}_{n=1}^{\infty}$ complete in $W_i^1(R^3)$, then the E-convergence of the SCF–RRM and MCSCF–RRM and the ψ-convergence of the SCF–RRM are ensured. However we remark that now, since we have orbitals restricted to being products of space and spin functions, the Ritz-energy E_m converges to a value E'_∞ which is the infimum of the energy functional on such a more restrictive class of orbitals and hence can be in general greater than the infimum E_∞ previously considered. Analogously, the Ritz-orbitals $(\psi_m^1, \ldots, \psi_m^N)$ are convergent to orbitals $(\psi_\infty'^1, \ldots, \psi_\infty'^N)$ which can merely be a local minimum and not a global minimum. The spatial part of the orbitals is expanded mostly in terms of Slater or Gauss functions [2]. However, a widespread belief [1, 2, 16–18] is that arbitrary orbital bases, as long as complete (on a topology which indeed is never specified, but understood to be that of $L_i^2(R^3)$), could be safely used without loosing the convergence of calculations. In virtue of the results of this work we can state that this belief is mathematically groundless. Klahn and Bingel [10] derived some sufficient conditions on the orbital exponents of Slater and Gauss functions, in order that sets of these functions turn out to be complete in $W^2(R^3)$ and hence in $W^1(R^3)$. Those conditions also ensure the E-convergence of the SCF–RRM and MCSCF–RRM as well as the ψ-convergence of SCF–RRM. In particular, when the set of Slater functions

$$\{r^l \exp[-\xi(n, l)r]Y_{lm}(\theta, \phi)\} \quad \text{for all } n \geq 1,\ l \geq 0,\ |m| \leq l \tag{16}$$

is taken as orbital basis, the above convergences are guaranteed if

(I) The sequences of positive numbers $\{\xi(n, l)\}_{n=1}^{\infty}$ have an accumulation point $\xi(l)$ with $0 < \xi(l) < \infty$ for each $l = 0, 1, 2, \ldots$.

When it is taken as orbital bases the set of Gauss functions

$$\{r^l \exp[-\xi(n, l)r^2]Y_{lm}(\theta, \phi)\} \quad \text{for all } n \geq 1,\ l \geq 0,\ |m| \leq l, \tag{17}$$

then the convergence of the SCF–RRM and MCSCF–RRM is guaranteed either if (I) holds or if

(II) the sequences $\{\xi(n, l)\}_{n=1}^{\infty}$ of positive orbital exponents for each l have a subsequence $\{\xi(n', l)\}_{n'=1}^{\infty}$ decreasing monotonically to zero with $\sum_{n'} \xi(n', l) = \infty$.

Recently [17, 18, 25] the problem of using extended bases built up from functions from the sets (16) or (17) has been investigated in atomic and molecular calculations. In those works the employment of such bases is made feasible because m_l

orbital exponents $\xi(n, l)$ of symmetry l are generated by means of the Raffenetti's formula [26]:

$$\xi(n, l) = \alpha_l \beta_l^n \qquad \alpha_l > 0, \qquad \beta_l > 1, \qquad n = 1, \ldots, m_l. \tag{19}$$

However, at variance with the Raffenetti's method the coefficients α_l and β_l are not determined by optimization, but either by a formula [18] in some way empirical, or quite arbitrarily [17, 25]. Anyway, in both cases it is supposed that such choices of α_l and β_l ensure the convergence of calculations. Now, in virtue of the above mentioned results (I) of Klahn and Bingel and in virtue of the results of the present work we can state that the convergence of SCF–RRM and MCSCF–RRM calculations by taking as orbital bases Slater or Gauss functions with orbital exponents generated by (19) is guaranteed whenever:

$$0 < \alpha_l < \infty \quad \text{and} \quad 0 < \beta_l \leq 1, \quad \text{for each } l. \tag{20}$$

Let us finally remark that the above condition on β_l is satisfied neither by the Raffenetti's formula (19), nor by the choices in [17, 18, 25]. However, as we said, the convergence might take place also with choices of β_l different from (20).

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