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$HF|f$ derivatives and Few Points Local Procedures

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Chimica fisica. — *Hf/f derivatives and Few Points Local Procedures.* Nota di GIANFRANCO MAJORINO, ALBERTO NAVA e ANGELO SIRONI, presentata (*) dal Socio M. SIMONETTA.

RIASSUNTO. — Dall'equazione di Schrödinger $Hu = Wu$ si ricava la condizione locale $\delta^K Hu/\delta x^K = W\delta^K u/\delta x^K$ (1), in cui x indica una qualunque coordinata elettronica. Questa condizione viene discussa:

a) In relazione al Lemma dei Momenti locali. Si dimostra qui che se una funzione f soddisfa alle (1) in un punto arbitrario p per ogni K ed x, allora essa è autofunzione di H.

b) In relazione alle Procedure Locali a pochi punti. Tali procedure vengono qui generalizzate mediante la formula $AHu(p) = WAu(p)$, essendo A un generico operatore.

Si giustifica così da un punto di vista teorico l'uso dell'operatore $A = 1$ per la costruzione delle funzioni di prova e l'uso di $A = \delta/\delta x$ come test di ottimizzazione di parametri.

Le nuove modalità di calcolo che derivano da questa analisi teorica sono state verificate con successo sui sistemi H ed H_2.

a) INTRODUCTION

The Few Points Local Procedures [1] consist in building up a wave function F satisfying a given number of analytic conditions in a given number of configurational points. These conditions are directly deduced from the Schrödinger equation $Hu = Wu$ and are certainly satisfied by its exact eigenfunctions u.

In this paper we intend to examine in particular the condition:

$$\delta^K Hu(p)/\delta x^K = W\delta^K u(p)/\delta x^K$$

(in which x is any electronic coordinate) in order to clarify two different points:

(i) Its connection with the well-known local conditions [2, 3, 4]: $H^K u(p) = WH^{K-1} u(p)$;

(ii) Its theoretical placing in a generalized Few Points Local Procedure.

These theoretical considerations can be easily checked both through atomic and through molecular computations.

In particular, a simpler local method than that proposed in [2] and a simpler convergence test than that proposed in [1] have been deduced and numerically checked with satisfactory results.

(*) Nella seduta del 10 aprile 1976.

b) DERIVATIVE CONDITIONS AND LOCAL MOMENT LEMMA

The so called Local Moment Lemma [2] states that if a function f satisfies in a given point p all the possible relations of the type $H^K f(p) = EH^{K-1} f(p)$, or, which is the same:

$$H^K f(p) = E^K f(p) \tag{1}$$

then f is an eigenfunction of H and E is the related eigenvalue.

Instead of (1) we can consider in p other relations of the type:

$$Hf^{(m)}(p) = Ef^{(m)}(p) \tag{2}$$

where m indicates a generic derivative along any direction.

A new Lemma can then be stated in which the conditions (1) are substituted by the conditions (2). More precisely, we can demonstrate the following theorem:

If a function f satisfies rel. (2) *for all the derivatives up to a given order* M *then relation* (1):

$$H^k f(p) = E^k f(p)$$

is also satisfied for all the integers $k < M/2 + 1$.

To demonstrate this it is convenient to rewrite (2) in the more detailed form (indicating with $q_1 \cdots q_w$ the electron coordinates):

$$(\delta^m Hf/\delta_{q_1}^{j_1} \cdots \delta_{q_w}^{j_w})_p = E\,(\delta^m f/\delta_{q_1}^{j_1} \cdots \delta_{q_w}^{j_w})_p$$

or, with obvious notations:

$$H_m^{j_1 \cdots j_w} = EF_m^{j_1 \cdots j_w} \tag{3}$$

(for any $0 < m < M$; for any integer $j_i > 0$ with $\sum_1^w j_i = m$).

Further more, from the general expression of the Hamiltonian operator:

$$H = -\sum_1^w \delta^2/2\delta q_i^2 + V(q_1 \cdots q_w)$$

it follows by inspection that its powers can be written as:

$$H^k = \sum_{m=0}^{2k} A_{j_1 \cdots j_w}^{(k)}\, \delta^m/\delta q_1^{j_1} \cdots \delta q_w^{j_w} \tag{4}$$

where for each m the sum is extended to all possible integers $j_1 + \cdots + j_w = m$.

The $A^{(k)}$ coefficients are obviously formed by the powers of the potential V and its derivatives.

Now, for a fixed $k < M/2$ we can multiply all the relations (3) where $m \leq 2k$ by the corresponding $A^{(k)}_{j_1 \cdots j_w}$; summing with respect to m we obtain:

$$\sum_{m=0}^{2k} A^{(k)}_{j_1 \cdots j_w} H_m^{j_1 \cdots j_w} = E \sum_{m=0}^{2k} A^{(k)}_{j_1 \cdots j_w} F_m^{j_1 \cdots j_w}.$$

From (3) and (4) it follows that this relation can be rewritten as

$$H^{k+1} f = E H^k f$$

where from rel. (1) can be deduced in a recursive way.

Taking into account the Local Moment Lemma, it follows that if in a given configurational point a function f satisfies rel. (2) for any k, then f is an *exact* eigenfunction of H, and E is the corresponding eigenvalue.

c) DERIVATIVE CONDITIONS AND FEW POINTS LOCAL PROCEDURE

The Few Points Local Procedure [1] can be generalized by applying an arbitrary operator A to both the members of the Schrödinger equation $Hu = Wu$. In a particular configurational point p we can then write:

$$AHu(p) = WAu(p)$$

so obtaining an infinite number of conditions certainly satisfied by the exact eigenfunctions u for any A and p. When A is a power of H we can then obtain the so called "Local Moment" relations [4, 5, 6] of the general type:

$$H^K u(p_i)/H^{K-1} u(p_i) = H^L u(p_j)/H^{L-1} u(p_j)$$

whereas for $A = \delta/\delta x$ (where x is an arbitrary direction) we obtain the relations discussed in the preceding paragraphs, which are not directly connected with the classical method of Moments [4, 7].

From a general point of view we can state the following theorem:

If $f_1 \cdots f_N$ *is a complete basis for a given eigenfunction* u, *then the problem of building up a linear combination* $F = \Sigma c_K f_K$ *isuch that*:

$$(5) \qquad AHF(p_1)/AF(p_1) = \cdots = AHF(p_N)/AF(p_N) = E$$

admit the solution $F = u$, $E = W$ *independently of the particular* $p_1 \cdots p_N$ *set.*

The demonstration can be easily obtained with the same procedure used in [1] for the particular case $A = 1$.

In this approach the problem of solving the Schrödinger equation is thus reduced to the problem of finding a different complete basis $f_1 \cdots f_N$ for each of its eigenfunctions. When the f_K set depends upon one or more adjustable parameters, we can utilize two different operators A_1, A_2 with the following procedure:

a) To fix a given parameter set and a given configurational point set;

b) To build up an F function satisfying the N relations (5) for the first operator A_1;

c) To evaluate the variability of the ratios $A_2\,HF\,(p_i)/A_2\,F\,(p_i)$ in the fixed $P_1 \cdots P_N$ set, e.g. through its variance around the mean value $\langle A_2 \rangle = N^{-1}\,\Sigma A_2\,HF\,(p_i)/A_2\,f\,(p_i)$ or around the E value obtained in *b*).

This variability can then be minimized both with respect to the configurational point set in which it is more convenient to perform the computations and with respect to the adjustable parameters.

This procedure can be theoretically justified by developing the function F in terms of exact eigenfunctions [6]: $F = \sum_{1}^{\infty} a_s\,u_s$. In fact this expression can be substituted in the ratio A_2HF/A_2F, so obtaining with further algebra:

$$A_2HF/A_2F = W_1 + \sum_{2}^{\infty} a_s\,A_2\,u_s\,(W_s - A_2HF/A_2\,F)/a_1\,A_2\,u_1 .$$

Thus it appears evident that the variability of the ratios $A_2\,HF/A_2\,F$ in the N configurational points depends upon the expansion coefficients a_s with $s > 1$. If the F function obtained with procedure *b*) is a good approximation of u_1, then the coefficients a_s with $s > 1$ are small, and we have in general a small variability.

Physically, with an obvious generalization of the considerations reported in [6], the energy error $W_1 - E$ can be written as:

$$W_1 - E = \sum_{N+1}^{\infty} (W_s - E)\,a_s\,D_s/a_1\,D \tag{6}$$

where:

$$D = \det \begin{vmatrix} A_1\,u_1\,(p_1) & \cdots & A_1\,u_N\,(p_1) \\ \cdots & \cdots & \cdots \\ A_1\,u_1\,(p_N) & \cdots & A_1\,u_N\,(p_N) \end{vmatrix}$$

and D_s is obtained substituting in D the function u_1 of the first column with the function u_s. It appears evident from (6) that the error in the energy depends upon the coefficients a_K with $K > N$. Furthermore, taking $A_1 = 1$ the elements of the D_s determinants are simply the values of the normalized u_s eigenfunctions in the configurational points p_k, which are in general very small numbers [6]. On the contrary, for $A_1 \neq 1$ the D_s determinants formed through the $Au_s\,(p_k)$ elements can assume in general arbitrarily big values. This is the case for instance of $A_1 = \delta/\delta x$, where the derivatives $\delta u_s\,(p_k)/\delta x$ can tend to infinite values. This seems to be a good argument to justify the particular choice $A_1 = 1$ of Ref. [1], and it can explain the numerical difficulties connected with the choice of $A_1 = H^K$ used in preceding approaches [2, 3, 4].

d) NUMERICAL EXAMPLES

It is obviously easier to evaluate the local values of the derivatives $Hf^{(m)}$ and $f^{(m)}$ (in an analytical as well as in a numerical way) than the Hamiltonian powers $H^k f$.

From this point of view the connection stated in section *b*) between LML and derivative conditions leads in an obvious manner to elaborating a numerical procedure which is in principle more convenient than that proposed in [3].

This connection has been checked on the hydrogen atom, starting from three 1s Slater type orbitals f_i with exponents 0.8, 1.1, and 1.2.

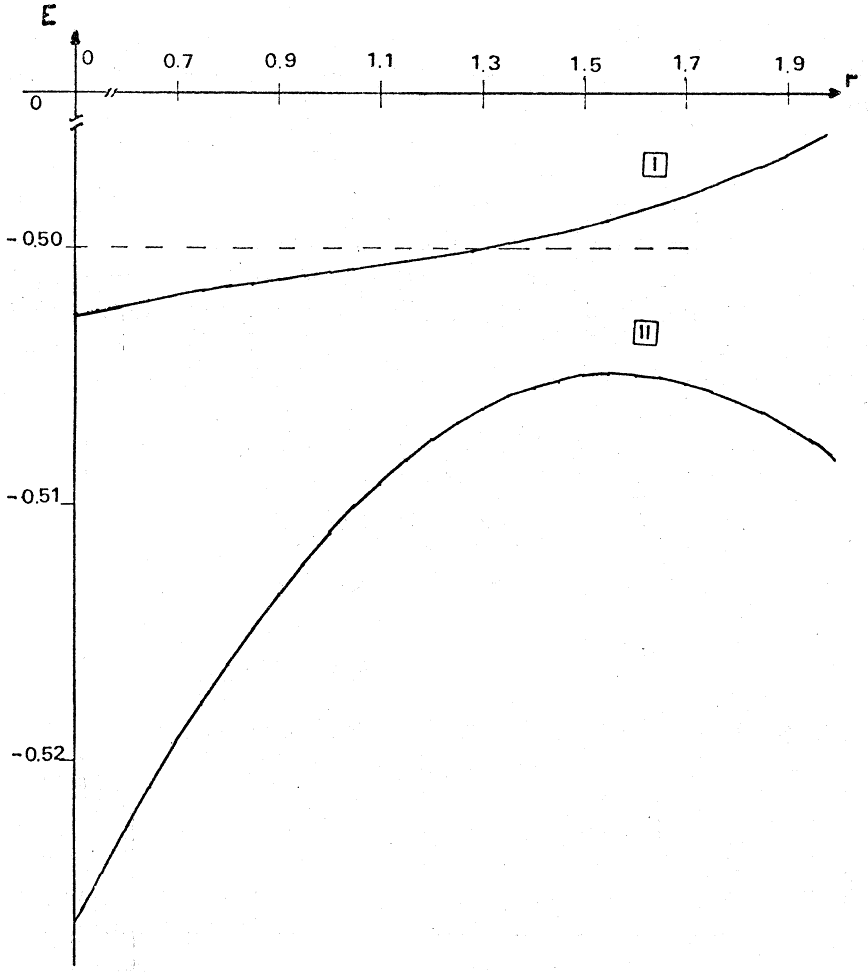

Fig. 1. – Hydrogen atom ground state energy evaluation repeating the calculations for $.6 < r < 2.0$ a.u. (I) present method, (II) L.C. method.

From this basis we built a function $f = \Sigma c_i f_i$, evaluating the c_i coefficients by the conditions:

$$(d^m \mathrm{H}f/dr^m)_p = \mathrm{E}\,(d^m f/dr^m)_p \qquad (m = 0\,, 1\,, 2)$$

taking care that the ground state is described by the only variable r.

Repeating the calculations for several points we obtained the plot of E *vs* r reported in fig. 1.

In each point the relation $\mathrm{H}^2 f/\mathrm{H}f = \mathrm{H}f/f = \mathrm{E}$ has been completely verified.

In fig. 1 we show also the graph obtained with the LC method [3] applied to the best couple of our trial functions.

A second set of computations has been made in connection with the considerations in section *c*). The main computational result of the general theory here presented is that *any measure* of the variability of the ratios $\mathrm{A}_2\,\mathrm{HF}\,(p)/\mathrm{A}_2\,\mathrm{F}\,(p)$ could in principle be used in order to optimize the parameters of a given trial function set $f_1 \cdots f_\mathrm{N}$. In a preceding paper [1] such variability has been evaluated on the H_2 system with the formula:

$$\mathrm{T}_2 = \sum_{\mathrm{K}=1}^{\mathrm{N}} \mathrm{D}_\mathrm{K}^2/\mathrm{F}_\mathrm{K}^2$$

where $\mathrm{D}_\mathrm{K}^2 = (\delta\,(\mathrm{HF}/\mathrm{F})/\delta p_1)_\mathrm{K}^2 + (\delta\,(\mathrm{HF}/\mathrm{F})/\delta p_2)_\mathrm{K}^2$ and p_1 and p_2 are the two electron positions of each point P_K. The disadvantage of this formula is that the F function must be normalized in order to compare different sets of trial functions.

Taking into account the considerations of section *c*) a new goodness test T has been checked under the form:

$$\mathrm{T} = (\Sigma \mathrm{D}_\mathrm{K}^2/\mathrm{F}_\mathrm{K}^2)/(\Sigma 1/\mathrm{F}_\mathrm{K}^2)\,.$$

TABLE I.

H_2 *energy evaluation (in a.u.) in 2 and 3 point computations for correlated functions of the type* $\mathrm{F} = \left(1 + \sum_{1}^{\mathrm{N}} c_\mathrm{K}\, r_{12}^{t_\mathrm{K}}\right)(1\,s_\mathrm{A} + 1\,s_\mathrm{B})_{1,2}\,(\alpha\beta - \beta\alpha)$. *The configurational point coordinates are* $\mathrm{P}_1 = \mathrm{P}_1\,(-\mathrm{X}\,, 0\,, 0\,, \mathrm{X}\,, 0\,, 0)$; *$d$ is the charge parameter of the* 1 *s orbitals.*

N	X	c_1	c_2	t_1	t_2	d	E	Error
2	1.8355	—0.0376	—	1.30	—	1.20	—1.23	6 %
3	2.0	0.0093	0.0070	3.20	3.32	1.20	—1.154	2 %

This test can be interpreted in the sense that the D_K^2 deviations (which are zero for the exact eigenfunction) must be weighted with the pounds $1/F_K^2$, or in the sense that the variations D_K^2 of the ratios HF/F must be evaluated in F_K^2 unities.

We used trial functions of the type [8]:

$$F = \left(1 + \sum_{K=0}^{N} c_K \, r_{12}^{t_K}\right) (1\, s_A + 1\, s_B)_1 (1\, s_A + 1\, s_B)_2 (\alpha\beta - \beta\alpha)$$

with $N = 1$ and $N = 2$. The results are reported in Table I; both the parameter X characterizing the electron position $P_1 = P_1(-X, 0, 0, X, 0, 0)$ and the t_K correlation exponents have been optimized by the T test.

In spite of the very small number of configurational points, the energy results are in good agreement with the theoretical value $E = -1.174$ a.u. for an internuclear distance of 1.4 a.u. [9].

Finally, several optimizations on the parameters of the bases of Ref. [1] have been performed with the T test.

In all the cases we obtained the same results as in [1], so confirming the theoretical considerations in section *c*).

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