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Gian Franco Majorino, Enrica Rusconi

Double scale factor method for minimization of molecular energy

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Chimica fisica. — *Double scale factor method for minimization of molecular energy.* Nota di GIAN FRANCO MAJORINO ed ENRICA RUSCONI, presentata (*) dal Corrisp. M. SIMONETTA.

RIASSUNTO. — Fissata una funzione d'onda di prova per una data molecola, si ricerca il minimo dell'energia molecolare al variare di un fattore di scala α per la funzione d'onda e di un fattore di scala $1/\beta$ per le distanze internucleari.

I valori di α e β sono ottimizzati per via analitica; si dimostra quindi che per tali valori l'energia cinetica e l'energia potenziale della molecola soddisfano il teorema del viriale.

Si rileva poi che, usando funzioni d'onda costruite con orbitali « centrati » (ad esempio orbitali di tipo Slater), questo metodo rappresenta una generalizzazione a molecole poliatomiche etero–nucleari del metodo degli orbitali fluttuanti.

È quindi riportata un'applicazione numerica per la molecola H_2, i cui risultati sono in completo accordo con quelli di lavori precedenti.

a) INTRODUCTION.

Starting from a trial wave function for a given molecule, it is possible to improve its energy value by scaling both the wave function and internuclear distances with the same proper scale factor. This is the well known procedure we shall call " single scale factor method ", expounded by Coulson and Bell [1] in 1945. The advantages of such a method are several.

From a theoretical point of view, when the total energy is minimized with respect to the scale factor, the virial theorem is automatically satisfied: in this way Lowdin [2] showed that an exact eigenfunction of any molecular hamiltonian in the Born-Oppenheimer approximation is such that the virial theorem is satisfied. From a numerical point of view, it suffices to calculate the kinetic and the potential energy of the molecule only once during all the minimization procedure.

We now propose to use two different scale factors, one for the wave function and one for the internuclear distances.

Optimizing both parameters we shall get an energy less than (or at the most equal to) that we can obtain with the single scale factor method. We pay for this advantage, from a numerical point of view, by calculating in several points the nuclear attraction. However it is well known that the computing time needed for this calculation is negligible compared with that needed for the electronic repulsion, which has to be calculated only once. Further we shall show that also with our method the virial theorem is satisfied.

(*) Nella seduta del 13 maggio 1967.

b) EXPOSITION OF THE PROCEDURE.

Let

$$H_1 = -1/2 \sum_i \nabla_i^2 - \sum_{in} Z_n/r_{in} + \sum_{i<j} 1/r_{ij} + \sum_{n<l} Z_n Z_l/r_{nl}$$

be the hamiltonian of a molecule with given nuclear configuration, where i, j label the electrons and n, l label the nuclei.

If we consider moreover a normalized trial wave function:

$$\psi_1 = \psi(r_1 \cdots r_N)$$

the following expectation values are determined:

Kinetic energy $\quad T_1 = -1/2 \sum_i \int \psi_1 \nabla_i^2 \psi_1 \, d\tau$

Electronic repulsion $\quad W_1 = \sum_{i<j} \int \psi_1 \, 1/r_{ij} \, \psi_1 \, d\tau$

Nuclear repulsion $\quad R_1 = \sum_{n<l} Z_n Z_l/r_{nl}$.

In addition we introduce another normalized wave function, obtained by scaling ψ_1 by a scale factor α:

$$\psi_\alpha = \alpha^{3N/2} \psi(\alpha r_1 \cdots \alpha r_N)$$

and the hamiltonian relative to the preceding nuclear configuration, after uniform stretch of all position vectors by a scale factor $1/\beta$:

$$H_\beta = -1/2 \sum_i \nabla_i^2 - \sum_{in} Z_n/r_{in\beta} + \sum_{i<j} 1/r_{ij} + \sum_{n<l} Z_n Z_l/r_{nl\beta}$$

where

$$r_{in\beta}^2 = (x_i - x_n/\beta)^2 + (y_i - y_n/\beta)^2 + (z_i - z_n/\beta)^2$$

$$r_{nl\beta}^2 = (x_n/\beta - x_l/\beta)^2 + (y_n/\beta - y_l/\beta)^2 + (z_n/\beta - z_l/\beta)^2.$$

Then it is easy to verify, with dimensional considerations like those used for example in [2], that the molecular energy corresponding to the nuclear configuration of hamiltonian H_β, calculated with the wave function ψ_α, results:

$$E(\alpha, \beta) = \alpha^2 T_1 + \alpha W_1 + \beta R_1 + \alpha f(\alpha/\beta)$$

where

$$f(\alpha/\beta) = \sum_{in} Z_n \int \psi_1 \psi_1 / \sqrt{(x_i - \alpha x_n/\beta)^2 + (y_i - \alpha y_n/\beta)^2 + (z_i - \alpha z_n \beta)^2} \, d\tau.$$

Indicating with γ the ratio α/β, $f(\gamma)$ represents the nuclear attraction calculated with the wave function ψ_1 associated with the nuclear configuration obtained by scaling the initial configuration by a scale factor γ.

The minimum conditions:

$$\partial E/\partial\alpha = 0$$

$$\partial E/\partial\beta = 0$$

using γ may be put into the form:

$$\gamma^2 \, df(\gamma)/d\gamma - R_1 = 0$$

$$2\,\alpha T_1 + W_1 + \gamma df(\gamma)/d\gamma + f(\gamma) = 0$$

$$\beta = \alpha/\gamma.$$

From an operative point of view it is useful to rewrite them as:

$$\gamma^2 \, df(\gamma)/d\gamma - R_1 = 0$$

$$\alpha = -\,[W_1 + R_1/\gamma + f(\gamma)]/\,2\,T_1$$

$$\beta = \alpha/\gamma$$

to emphasize that the first equation gives the value of the ratio γ which, when substituted in the second and then in the third equation, allows us to calculate immediately the parameter values α and β minimizing $E(\alpha, \beta)$.

c) Connection with the floating orbital procedure.

If the function ψ_1 is built with a Slater type orbital basic set, it is easy to verify that, calling r_m the coordinates of a generic orbital centre, and δ_k the exponent of the *k–th* atomic orbital, we have:

$$\psi_\alpha = \alpha^{3N/2}\,\psi\,(r_m \mid \delta_k \mid \alpha r_i) = \psi_{\text{NORM}}\,(r_m/\alpha \mid \alpha\delta_k \mid r_i)$$

where NORM indicates that the function is normalized.

The meaning of the energy $E(\alpha, \beta)$ in this case is made clear as follows. If we take a given nuclear configuration (r_n), an orbital centre configuration and orbital exponents (r_m, δ_k)—i.e., if we fix some floating orbitals [3] [4] [5] [6]—the energy $E(\alpha, \beta)$ is the energy associated with the nuclear configuration (r_n/β) and the orbital configuration $(r_m/\alpha, \alpha\delta_k)$.

It is worth noting that—fixing in a suitable way the coordinate origin, and eventually repeating the preceding procedure with different coordinate systems—one can pass from a given nuclear and orbital configuration to any other nuclear and orbital configuration. That is, one can make the nuclei and centres "floating" in the space in a completely arbitrary way, each new configuration being entirely characterized by a parameter pair (α, β); at each stage only the nuclear attraction $f(\gamma)$ must be recalculated.

However, the exponents δ_k are to be multiplied by the same constant α which divides the coordinates r_m: this is the only effective restriction of the procedure. Fig. 1 shows how the final configuration (for fixed α and β) chan-

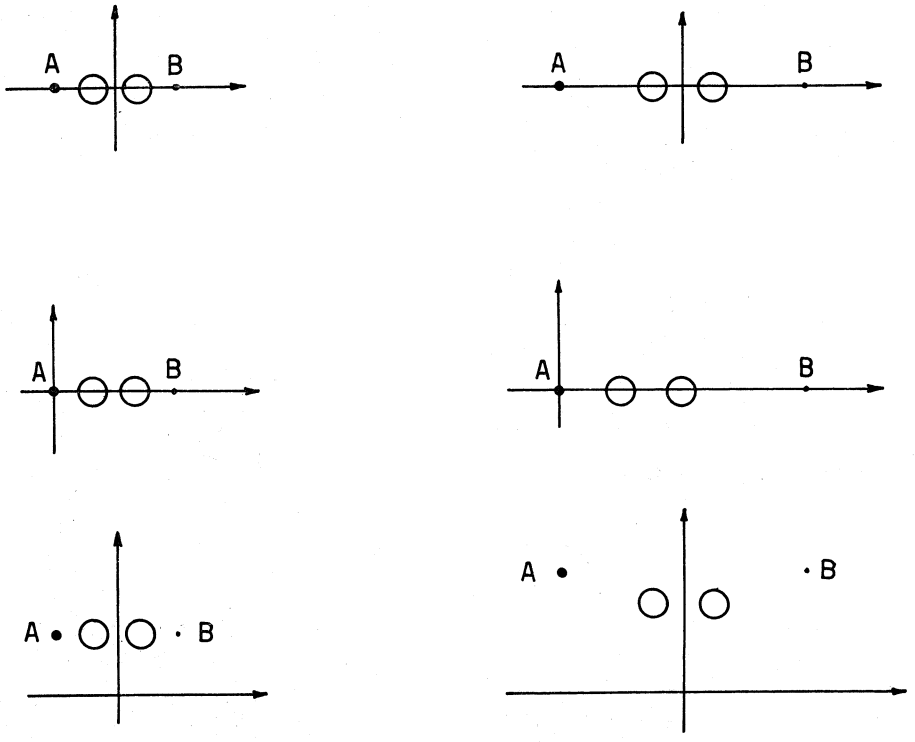

Fig. 1. – On the left there is the same nuclear and orbital initial configuration ($\alpha = \beta = 1$); on the right the corresponding configurations with $\alpha = 3/2$, $\beta = 1/2$ in three different coordinate systems.

The points A and B label the nuclei, the circles represent 1 *s* Slater type orbitals.

ges in varying the origin of the coordinate system. This possibility can be used with molecules built of different atoms: for example, in an etheronuclear biatomic molecule we do not know if the best energy is obtainable by fixing the origin in the middle point, or in the center of mass, or coincident with one of the two nuclei of the molecule. Both the energy and the function $f(\gamma)$ should be indicated with $E_0(\alpha, \beta)$ and $f_0(\gamma)$ to point out their dependence on the origin of the coordinates.

d) CONNECTION WITH THE VIRIAL THEOREM.

It has been demonstrated [1], [2], [7] that an optimum scale factor function gives values of the kinetic energy T and of the potential energy V which satisfy the virial theorem:

$$V = -2T.$$

In the case of the double scale factor, the optimization procedure with respect to α is achieved subordinately to the determination of the optimum value of the parameter $\gamma = \alpha/\beta$: yet, we can demonstrate that when $E(\alpha, \beta)$ is minimum, the virial theorem is automatically satisfied.

At first we observe that optimizing a wave function with a scale factor s is equivalent to applying the double scale factor procedure with the supplementary condition $\alpha = \beta = s$; in fact we have:

$$E(s, s) = s^2 T_1 + sW_1 + sR_1 + sf(1) = s^2 T_1 + sV_1$$

which leads to the well known minimum condition:

$$2sT_1 + V_1 = 0 .$$

In second place, let us assume that we have calculated two values $\bar{\alpha}$ and $\bar{\beta}$ such that:

$$E(\bar{\alpha}, \bar{\beta}) = \text{minimum.} \tag{1}$$

If now we optimize the function $\psi_{\bar{\alpha}}$ with respect to the scale factor s, we get a value $\bar{s}$ such that:

$$E(\bar{s}\bar{\alpha}, \bar{s}\bar{\beta}) = \text{minimum.} \tag{2}$$

From (1) and (2) it results $\bar{s} = 1$. That is, $\psi_{\bar{\alpha}}$ is already an optimum function with regard to the scale factor, and the virial theorem is then automatically satisfied.

e) Numerical application.

The preceding procedure has been used to investigate the minimum energy configuration of the H_2 molecule, employing as wave function:

$$\psi = N(1s_a\, 1s_b + 1s_b\, 1s_a)$$

in order to compare the results with those reported in [3] and [4]. We have taken nuclear and orbital initial configurations as coincident ($r_m = r_n$), putting the two nuclei 1.406 Å apart. The calculations were repeated with different values of initial orbital exponent δ; the results are reported in the Table I.

The minimum of the energy is found to be 1.1444 a.u. with internuclear distance of 1.410 Å, nuclei-orbital centre distance of 0.05454 Å and exponent $\delta = 1.167$. These values are equal to those reported in [4].

At each stage the virial theorem is satisfied.

About the minimization methods used in the mentioned papers, we note that, for the H_2 molecule, Hurley [6] suggests a minimization procedure on two variables, which offers the advantage of fixing the nuclear configuration

TABLE I.

H_2 *molecule with* $\psi = N(1s_a\,1s_b + 1s_b\,1s_a)$ *and initial orbital and internuclear distance* $R = 1.406$ Å.

In the first column there is the initial exponent; then α and β optimum values and corresponding: exponent δ, orbital distance R_0, nuclear distance R_n, total energy $E(\alpha, \beta)$.

$\delta_{INIZ.}$	α	β	δ	R_0	R_n	E
0.80	1.42615	1.11520	1.1409	0.9859	1.2608	—1.12661
0.90	1.28248	1.07920	1.1542	1.0963	1.3028	—1.13709
1.00	1.16313	1.03582	1.1631	1.2088	1.3574	—1.14298
1.08	1.08053	0.99696	1.1670	1.3012	1.4103	—1.14438
1.10	1.06135	0.98612	1.1675	1.3247	1.4258	—1.14430
1.20	0.97295	0.93268	1.1675	1.4451	1.5075	—1.14124
1.30	0.89521	0.87660	1.1638	1.5706	1.6039	—1.13509

we wish to reach, but his formulas are tied to the particular wave function used and to the particular geometry of the biatomic homonuclear molecule.

For the H_3^+ ion, Barker and others [5] used a minimization procedure involving in an analytical way only the orbital exponent.

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