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A Modified del Re Method*

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A modified computational Del Re procedure is exposed. The method allows the user to spare a large amount of time and storage, together with the possible study of large molecules up to two hundred atoms or more.

Del Re's method [3] has been utilized successfully to study various problems in Quantum Chemistry [4–7]. Due to its simplicity, in some cases, as the qualitative treatment of biological polymers, it can substitute advantageously the present empirical methods. However, the original formulation of Del Re presents some problems which this work pretends to clarify.

The fundamental concept of the method rests on the Coulomb integral of each atom A:

$$\alpha_A = \alpha_0 + \delta_A \beta_0 .$$

For the evaluation of the parameters δ_A for each atom a linear system of equations is constructed

$$\delta_A = \delta_{0,A} + \sum_B \gamma_{AB} \delta_B , \tag{1}$$

where $\delta_{0,A}$ and γ_{AB} are constants, which can be found in the literature [1, 3, 4] and where the sum $\sum_B$ refers to all the atoms linked to A.

The solution of a system like Eq. (1) for large molecules presents a considerable limitation in using the method. Furthermore, the quantities γ_{AB} are not symmetrical, in general $\gamma_{AB} \neq \gamma_{BA}$. Our first task will be the resolution of system (1) without making necessary a matrix inversion.

The system (1) can be expressed in matrix form

$$\delta = \delta_0 + \Gamma \delta , \tag{2}$$

δ, δ_0 being two column vectors whose elements are the unknowns δ_A and the initial parameters $\delta_{0,A}$ respectively; Γ will be a matrix with the parameters γ_{AB} as elements and zeros in the A-row sites, which do not correspond to atoms bounded directly to A. A rearrangement of (2) gives

$$(I - \Gamma)\delta = \delta_0 , \tag{3}$$

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where I is the unit matrix. In this form the desired solution of system (1) will be obtained by means of

$$\delta = (I - \Gamma)^{-1} \delta_0 . \tag{4}$$

To avoid the inversion of the $I - \Gamma$ matrix, the fact can be utilized that the inverse can be expanded as a power series of Γ

$$(I - \Gamma)^{-1} = \sum_{i=0}^{\infty} \Gamma^i . \tag{5}$$

Then the solutions of (4) can be calculated by

$$\delta = \delta_0 + \sum_{i=1}^{\infty} \Gamma^i \delta_0 . \tag{6}$$

Taking $\delta = \delta_0$ as initial step and substituting in the right hand side of (2), the following iterative chain can be found

1st step $$\delta_{(1)} = \delta_0 + \Gamma \delta_0 , \tag{7a}$$

2nd step $$\delta_{(2)} = \delta_0 + \Gamma \delta_{(1)} = \delta_0 + \Gamma \delta_0 + \Gamma^2 \delta_0 , \tag{7b}$$

nth step $$\delta_{(n)} = \delta_0 + \Gamma \delta_{(n-1)} = \delta_0 + \sum_{i=1}^{n} \Gamma^i \delta_0 , \tag{7n}$$

evidently, the sequence $\{\delta_{(K)}\} \to \delta$ when $K \to \infty$, so that Eq. (7n) corresponds to (6) for $n = \infty$.

At this stage, the utility of the iterative procedure must be shown by a convergence criterion for Eq. (6). In fact, calling Δ_K the difference

$$\Delta_K = \delta_{(K)} - \delta_{(K-1)} = \Gamma^K \delta_0 ,$$

the convergence criterion will be

$$\Delta_K \to 0 \quad \text{if} \quad \Gamma^K \to 0 ,$$

Therefore the series will be convergent if the spectral radius of Γ, $\varrho(\Gamma)$, can be found in the open interval [2]

$$0 < \varrho(\Gamma) < 1 .$$

The sufficient condition for a matrix to be regular is such that the matrix must be diagonally dominant [2], this condition in our case can be written

$$\sum_{J(\neq I)}^{M} \gamma_{IJ} = \varrho_I < 1, \qquad (I = 1, M) ,$$

M^2 being the dimension of $I - \Gamma$.

As a consequence of Gerschgorin's theorem [2]

$$\varrho(\Gamma) \leqq \max_I (\varrho_I) ,$$

hence

$$\varrho(\Gamma) < 1 ;$$

and the convergence can be assured.

Having solved in this way the convergence problem, the dimension of the matrices may be a limitation for the application of the method. To reduce about one third of the size of the problem, one can use the Eq. (1) corresponding to the atoms X, which have only one bond to another atom A.

$$\delta_X = \delta_{0,X} + \gamma_{XA}\delta_A\,, \tag{8}$$

substituting (8) in the expression (1) of atom A, that equation can be rewritten

$$\delta_A = \delta_{0,A} + \sum_B{}' \gamma_{AB}\delta_B + \sum_X \gamma_{AX}\delta_X\,, \tag{9}$$

where $\sum_B{}'$ runs over the atoms linked to A and also to some other atom, and $\sum_X$ runs over the atoms linked only to A, one obtains

$$\delta_A = \lambda_A + \sum_B{}' \mu_{AB}\delta_B\,, \tag{10}$$

with

$$\lambda_A = \left(\delta_{0,A} + \sum_X \gamma_{AX}\delta_{0,X}\right)\omega_A^{-1}\,,$$

$$\mu_{AB} = \gamma_{AB}\omega_A^{-1}$$

and

$$\omega_A = 1 - \sum_X \gamma_{AX}\gamma_{XA}\,.$$

The system (10) is similar to (1), and can be solved with the same iterative procedure, because the matrix M with elements μ_{AB} can be obtained from Γ with the transformation

$$M = P\Gamma Q^{-1}\,.$$

P and Q are regular matrices, formed by products of elementary matrices, related to the substitutions which have been used to construct system (10). Then, if the sequence $\{\Gamma^K\}\to 0$, also $\{M^K\}\to 0$ [2].

Resuming, the procedure can follow the steps

a) Build up system (1).

b) Transform the system (1) into system (9).

c) $\delta = \delta_0$.

d) With (9), after substitution, find the new δ's.

e) Observe if between two iterative steps the difference $|\delta_{(K),A} - \delta_{(K-1),A}|$ lies in some given range.

f) If so, end the procedure; if not go to d).

In practice, for an absolute error of 10^{-5} between two iterations, the convergence is obtained in a few steps. The procedure has been tested with amino-acids already calculated [4], and the absolute mean error found in the net charges is of the order of 10^{-3}.

At the same time, calculations have been carried out on a great variety of compounds: steroids, alkaloids and polypeptides; the capacity of the treatment has been tested on the insulin molecule (777 atoms).

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