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Approximate LCAO-SCF methods: reliability of the total energy calculation

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Chimica. — *Approximate* LCAO-SCF *methods: reliability of the total energy calculation.* Nota di Giovanni Ciullo, Antonio Sgamellotti, Fausto Casagrande e Mario Morcellini [*], presentata [**] dal Socio G. Sartori.

Riassunto. — Sono illustrate le difficoltà del calcolo dell'energia totale in un metodo LCAO–SCF semplificato dall'uso estensivo di approssimazioni tipo Mulliken e da alcune approssimazioni di carica puntiforme. Non appare possibile interpretare in tale metodo il rilassamento elettronico durante la ionizzazione. Viene elaborato un criterio generale per stabilire la possibilità di dare un senso quantitativo al calcolo dell'energia totale nei metodi LCAO–SCF approssimati.

A theoretical investigation has recently been carried out in this laboratory on the electronic structure of a series of nickel(II) complexes with bidentate sulphur ligands, containing the planar [NiS$_4$] chromophore, by the use of an LCAO-MO-SCF method [1]. The method of calculation is an extension of that reported by Hillier *et al.* [2, 3], and is based on some numerical approximations for the matrix elements of the Roothaan SCF operator, without any empirical *a posteriori* parameter being introduced, so that it is suitable for extensive applications to coordination compounds. By applying Mulliken-type approximations to the electronic interaction integrals and a point charge approximation to the whole interaction with the charge of an atom, the diagonal and off-diagonal matrix elements become simplified:

(1)
$$F_{aa} = \varepsilon_a - \sum_{B \neq A} q_B A_{aB} ,$$

(2)
$$F_{ab} = S_{ab} (\varepsilon_a + \varepsilon_b) - T_{ab} - \tfrac{1}{2} S_{ab} \sum_{C \neq A, B} q_C (A_{aC} + A_{bC}) .$$

ε_a is the atomic energy of the orbital a belonging to the atom A, with charges derived by the Mulliken population analysis except for the replacement of the population n_a of the orbital a with $(1 + n_a/2)$; S_{ab} and T_{ab} are the overlap and kinetic integrals, respectively; q_B is the total charge of the atom B; A_{aB} is the interaction of an electron in the orbital a with a point charge placed at the centre of the atom B. All the integrals S_{ab}, T_{ab}, A_{aB} are computed theoretically, while ε_a may be calculated by empirical one-centre integrals [4]. To ensure rotational invariance [5], the quantities ε_a, ε_b, A_{aC} and A_{bC} are averaged, only in equation (2), over the orbital sets with the same quantum numbers n and l. The electronic transition energies are not computed as simple difference of the eigenvalues, but the difference is corrected by the appropriate Coulomb and exchange molecular integrals.

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These are, however, calculated without increasing the analytical difficulties involved in the equation (1) and (2). It should be noticed that the definition of the one-centre part ε_a is different from that used by Hillier [2]. Only our definition, which is more theoretically correct, permits application of interelectronic corrections in computing the transition energies, obtaining non negative values and energies of the right order of magnitude.

The calculations, performed by this method on the nickel(II) dithio-complexes, give a good interpretation of the electronic structure and a satisfactory assignment of the electronic transitions [1]. This paper reports the failure of the method in an other application. The reasons of the failure are investigated, and the important conclusions reached are generalised to the validity of the approximate MO methods. From the sequence of the eigenvalues, it is found that the highest occupied molecular orbitals are localised on the ligands and are of both u and g symmetry. However the transition energies of the mainly $3d$ orbitals turn out to be the lowest ones via the interelectronic interaction corrections. As far as the ionization energies are concerned, some ab initio calculations on coordination compounds [6, 7] have shown an increase of the energies of the chiefly $3d$ orbitals with respect to the ligand ones, when, going beyond Koopmans' theorem [8], the difference between the total energies of the ionized SCF polyelectronic state and of the ground one is computed. In attempting to test the same procedure, the problem of the calculation of the total energy arises in the framework of the present MO method.

Considering the ionization of an orbitally non degenerate orbital, we use the rigorous expression of the energy for a monodeterminantal wave-function of closed shell or doublet type:

$$(3) \qquad\qquad E_T = \sum_i n_i \left(e_i - 0.5\, B_i \right) .$$

n_i, e_i and B_i are, for molecular orbital i, the occupation number, the eigen-value and the total interaction with the whole electronic charge of the molecule described by the SCF molecular orbitals. To clarify the significance of B_i, it may be noted that the following formula holds:

$$e_i = h_{ii} + B_i ,$$

where h_{ii} is the diagonal matrix element of the core part of the molecular SCF operator. Of course, (3) arises from the need to subtract the electronic part of the total energy from the sum of the eigenvalues of the occupied orbitals. To compute B_i, extensive use of the Mulliken approximation leads to a linear combination of the atomic Coulomb integrals J_{ab}, which do not appear explicitly in the matrix elements (1) and (2). In order not to increase the analytical difficulties met with in computing (1) and (2), the following two approximations are utilised for J_{ab}:

$$(4) \qquad\qquad J_{ab} = \frac{A_{aB} + A_{bA}}{2} ,$$

or

(5)
$$J_{ab} = A_{aA} + A_{bB} - \frac{1}{R_{AB}},$$

where R_{AB} is the distance between A and B (in a.u.). The results are almost the same, but in both cases are not satisfactory. The orbitals, in the ionization process, change compositions, so confirming the non applicability of Koopmans' theorem, but the ionization energies increase with respect to the Koopmans value. In other words, the total SCF energy of the ionized state is larger than that of the state ionized according to the Koopmans' theorem: i.e. the energy is not at a minimum value. In our opinion, this occurs because the total energy is not calculated in a way conforming to the algorithms used in (1) and (2). It is easy to note that neither equation (4) nor (5) correspond to the calculation of J_{ab} implicitly contained in (1) and (2); rather, in this case, it is impossible to extract a uniform treatment for the integral J_{ab} from (1) and (2). In fact, even neglecting the exchange terms and considering the two-centre interactions as entirely Coulomb ones, it may be derived, from (1) and (2), that J_{ac} is calculated as A_{aC} in F_{aa} or in F_{ab}, but as A_{cA} in F_{cc} or in F_{cb}. Further, because of the requirement of the rotational invariance, the integrals A_{aC} are averaged in (2) but not in (1). Even the Mulliken approximation is not always applied. In fact, an analysis of the origin of equation (2) leads to the conclusion that, in the off-diagonal elements, the charge distribution ab is approximated by $S_{ab} \cdot aa$, when it interacts with orbitals belonging to atom A, and by $S_{ab} \cdot bb$, if the charge distribution interacts with orbitals of atom B. Thus, it is impossible to express conveniently the interelectronic interaction, because it is not dealt with in an analogous way in formulae (1) and (2).

To calculate the total energy in a way conforming to (1) and (2), the problem could be shifted to the calculation of the core energy instead of the electronic one. The equation (3) may be rewritten:

(6)
$$E_T = 0.5 \sum_i n_i (e_i + h_{ii}).$$

For the core matrix elements h_{aa}, h_{ab}, we have used formulae completely analogous to (1) and (2), derived in the same way. In these formulae, ε_a and ε_b are replaced by u_a and u_b, where the interaction with the valence electron charge of A and B, respectively, is lacking and only the interaction with the cores is considered. Further, the core charges of atoms A, B and C appear in place of q_A, q_B and q_C. The results of calculations, performed utilising equation (6), are better, but the ionization energies are still larger than those obtained by Koopmans' theorem.

Even in this case, it is clear that we are enable to separate the appropriate core energy from (1) and (2). In fact, to derive (1) and (2), the following equation has been utilised:

(7)
$$(T + V^A) a = \varepsilon_a a,$$

where V^A is the potential energy due to the whole atom A, with occupation numbers obtained from the Mulliken population analysis. To obtain analogous equations for h_{aa} and h_{ab}, we must use the formula:

$$(8) \qquad (T + U^A)\, a = u_a\, a \,,$$

where in U^A only the interaction with the core of A remains. Clearly, equation (8) is much more incorrect than (7), since the eigenfunction a refers rather to the electronic structure resulting for atom A, i.e. about electrically neutral; whilst U^A is determined by the core charge, which may be even notably positive. So, by the use of (8), the appropriate core energy cannot be separated from the total energy.

It turns out that the formulae of the matrix elements must contain a precise separation between the core part and the electronic one, so that each of them may be clearly defined. This is then a criterion of validity for the approximate LCAO-SCF methods. There are, indeed, several such methods, due to the intrinsic difficulties of coupling the feasibility of calculations with the reliability of results. For a long time, quantum chemistry investigations have been concerned with approximate methods, especially in the fields of coordination compounds and of large organic systems. The several approximations, apart from being judged on the basis of their intrinsic validity and the reliability of the results obtained, have also been conditioned by the requirement of ensuring a rotational or hybridizational invariance of the results. The novel criterion refers only to the use of total energy in comparing different states, in the sense that it does not take into account other results or other applications; i.e. a method like that reported in this paper, which does not satisfy that criterion, may be more accurate, so far as other applications are concerned, than a method satisfying it. The criterion may be summarised thus: the approximations utilised in computing the total energy must correspond to those used for the matrix elements. We have also pointed out that a necessary condition for this correspondence is the exact separation between the core parts and the electronic ones of the matrix elements.

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