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A METHOD TO IMPROVE ENERGIES FROM THE ZERO OVERLAP APPROXIMATION

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With modern computing facilities the simplification resulting from the use of zero-differential-overlap models is not very significant, at least in a great number of molecular systems. So deriving from the energies obtained with the zero overlap model,as a basis,more accurate ones, nearer to those which could be obtained with a model including overlap, is no more a crucial problem, as it wasin the thirties when the secular determinants had to be solved by hand.* Nevertheless a theoretical problem is never old-fashioned. We should like to show in that paper, from a very simple first order perturbation treatment and an iterative process, that it is possible to derive a formula improving the energies obtained within the frame of the zero overlap model, not only when there is one overlap integral, as in the Wheland method (1)(2), but also whatever the number of overlap integrals may be.

Let ψ_k° be the monoelectronic wave function corresponding to some particular unperturbed non degenerate level with energy E_k° . The wave function is written as a linear combination of atomics orbitals :

$$\psi_k^\circ = \sum_i C_{ik}\chi_i$$

We introduce the influence of overlap as a first order perturbation $-E_k^\circ S_{ij}$ to the H_{ij}° integrals, since in the zero overlap approximation the terms $H_{ij}^\circ - E^\circ S_{ij}$ are replaced by H_{ij}°. The energy E_k° is the best value to use in the perturbation term for the particular level under examination. The unperturbed state has an integral H_{ij}° ,

the perturbed one $H_{ij} = H^{\circ}_{ij} + H^{1}_{ij}$ with $H^{1}_{ij} = \langle\chi_i|H^1|\chi_j\rangle = - E^{\circ}_k S_{ij}$.
The first order correction to the energy level k is $E^1_k = \langle\psi^{\circ}_k|H^1|\psi^{\circ}_k\rangle$ where H^1 is the perturbation term to the hamiltonian.

ψ°_k is replaced by its linear combination. We retain only the terms which have a non zero value. These terms are those which introduce a perturbation to the H°_{ij} integrals. That is to say those where two different atomic orbitals are involved. E^1_k becomes :

$$E^1_k = 2\sum_{\substack{i,j \\ i\neq j}} C_{ik}C_{jk} \langle\chi_i|H^1|\chi_j\rangle$$

where χ_i and χ_j are the atomic orbitals involved in an overlap. Replacing the integrals by their values $- E^{\circ}_k S_{ij}$, the correction to the unperturbed state is written :

$$E^1_k = -2\, E^{\circ}_k \sum_{\substack{i,j \\ i\neq j}} C_{ik}C_{jk}S_{ij}$$

$$E^1_k = -E^{\circ}_k\, \sigma \qquad \text{with} \quad \sigma = 2\sum_{\substack{i,j \\ i\neq j}} C_{ik}C_{jk}S_{ij}$$

The energy ε_k , for a level k, taking the perturbation into account is then :

$$\varepsilon_k = E^{\circ}_k + E^1_k = E^{\circ}_k - E^{\circ}_k\sigma = E^{\circ}_k\,(1-\sigma)$$

In a system with two atomic orbitals and S_{ij} being 0,27, the correction to E°_k is the factor 0,73 for the bonding combination, and 1,27 for the antibonding one. The values obtained when using explicitely the overlap are 0,79 and 1,37. The correction is promising when considering the crudeness of the method. Furthermore it is possible to get it better.

The value ε_k is better than E°_k . We have to use that new value to improve the perturbation term. Instead of being $- E^{\circ}_k\,\sigma$ that perturbation term will be $- \varepsilon_k\,\sigma$, that is to say : $- E^{\circ}_k\,(1-\sigma)\sigma$.
The energy of the perturbed state becomes :

$$E^{\circ}_k\left[1-\sigma(1-\sigma)\right]$$

A new iteration leads to :

$$E^{\circ}_k\left[1-\sigma\left[1-\sigma(1-\sigma)\right]\right]$$

Where E°_k is multiplied by $(1-\sigma+\sigma^2+\sigma^3)$. An infinite number of iterative cycles shows that E°_k in fact is multiplied by:

$1 - \sigma + \sigma^2 - \sigma^3 + \ldots + (-1)^n \sigma^n + \ldots$ whose value is $\frac{1}{1+\sigma}$ with $\sigma<1$.

Letting drop the perturbation labelling we can say that after the perturbation treatment and the iterative process an energy ε_k is obtained for a level k; that energy is better than the value E_k calculated assuming the zero overlap approximation :

$$\varepsilon_k = \frac{E_k}{1 + \sigma}$$

with $\sigma<1$ and $\sigma = 2 \sum_{\substack{i,j \\ i\neq j}} C_{ik} C_{jk} S_{ij}$ where C_{ik} and C_{jk} are the coefficients in the zero overlap approximation, related to the atomic orbitals χ_i and χ_j. These atomic orbitals are those which, in the LCAO expansion of ψ_k, are involved in an overlap. That formula does not limit the number of overlap integrals to take into account.

One could check for the above system of two atomic orbitals, that our treatment gives the exact theoretical values. With the two possible combinations $\psi_1 = \frac{1}{\sqrt{2}} (\chi_1 + \chi_2)$ and $\psi_2 = \frac{1}{\sqrt{2}} (\chi_1 - \chi_2)$ we obtain

$$\varepsilon_1 = \frac{E_1}{1 + S} \qquad \varepsilon_2 = \frac{E_2}{1 - S}$$

since $\sigma_1 = 2 (\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}}) S = S$ and $\sigma_2 = 2 (\frac{1}{\sqrt{2}})(-\frac{1}{\sqrt{2}}) S = - S$.

When considering more complex systems, those which can be studied by the Wheland method (with one type of overlap), the formula gives the same results as those obtained when taking explicitely the overlaps into account. That accuracy is not surprising since the crudeness of the first order perturbation treatment is improvedby the iterative process. For systems with several different overlaps the formula will lead to much better values than in the zero overlap approximation.

The formula hasbeenestablished in the case of non degenerate levels. In fact, when trying to improve the energies obtained in the zero overlap approximation we are not concerned by removing the degeneracy. Each level is studied for its own energy value and the above formula may be used. Logically we should have the same correction for each level of a degenerate system. One can check that point on

simple molecular entities such as three equivalent atomic orbitals, or on the p_π orbitals of a benzene nucleus. We obtain the same results as those obtained when including rigorously the overlap in the Wheland method.

REFERENCES

1) G.W.WHELAND J.Amer.Chem.Soc. 63,2025(1941)

2) I.N.LEVINE "Quantum Chemistry" Volume I : Quantum Mechanics and Molecular Electronic Structure . Allyn and Bacon, Boston 1970,p 534

* Furthermore it has been known since that time, that the inclusion of overlap, at least in π-systems of organic molecules, does not lead to values in much better agreement with experiment. The neglect of overlap is often justified by the empirical success of the simple HMO procedure, or even by the success of more advanced MO methods in which electron repulsion terms are taken into account

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