On the Use of Atom-Localized Molecular Orbitals

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Atom-localized molecular orbitals are defined and discussed for alternant hydrocarbons, in the HMO approximation.

It has been observed that the pi orbitals of benzene [1] and some other molecules [2] can be localized on atoms. These atom-localized molecular orbitals (ALMO's) can be defined in a more general way. We propose to define them as the molecular orbitals (MO's) which maximize the contribution to the electronic charge density of atoms (or sets of atoms) which are assigned to the MO's:

$$\sum_i \sum_m^i c_{mi}^2 \quad \text{— maximum},$$

where c_{mi} is the coefficient of the atomic orbital (AO) m in the MO i, and

i above $\sum$ symbolizes the limitation to the AO's assigned to the MO i.

Such ALMO's can be obtained directly, such as in [3, 4], or by unitary transformations among MO's of other types. In this case the transformation relationships can be obtained by particularizing those of the more general localization definition [5, 6]:

$$\sum_i \sum_{m,n}^i c_{mi} c_{ni} M_{mn} \quad \text{— extreme},$$

where M is a matrix that defines localization.

In the pi approximation, when localized on the starred atoms of alternant hydrocarbons [7], the AO coefficients of the ALMO's are given by:

$$c_{mi} = \begin{cases} 1/\sqrt{2} & \text{if } m = m_i \text{ (MO } i \text{ is localized on } m_i\text{)}, \\ 0 & \text{if } m \neq m_i, \text{ starred}, \\ P_{mm_i}/\sqrt{2} & \text{if } m \text{ is unstarred} \end{cases}$$

(P is the bond order and charge density matrix).

An alternation of the sign of c_{mi} (m-unstarred) can be observed. In the HMO [8] approximation only atoms adjacent to m_i contribute to the bonding energy (the other coefficients on unstarred atoms ensure orthogonality). It follows that the ALMO energy can be defined as:

$$E_i = \alpha + \beta(\sqrt{3} - F_{m_i}),$$

where F_{m_i} is the free valence number [9], giving the total energy:

$$E = \sum_i E_i .$$

Virtual ALMO's can be defined from virtual MO's. They differ from the occupied ALMO's only by the sign of the AO coefficients on the unstarred atoms. Their energy is:

$$E_{i*} = \alpha - \beta(\sqrt{3} - F_{m_i}).$$

The ALMO's could provide an useful tool in processes where only some centers are involved. The mathematical foundation for such a treatment is given by the perturbation theory. The great number of zero coefficients in ALMO's simplifies considerably the perturbation formulas. By using a technique, that is adapted to a localized MO treatment [4, 10–14], the well-known formulas can be found (up to second order):

$$E^{(0)} = 2 \sum_i E_i ,$$

$$E^{(1)} = 2 \sum_i \langle i | v | i \rangle ,$$

$$E^{(2)} = 2 \sum_{i,j*} \langle i | v | j^* \rangle^2 (E_i - E_{j*})^{-1} ,$$

v being the one-electron perturbation operator. Simple formulas can be obtained, e.g. in the case when the perturbation is:

a) monocentric $\delta\alpha_r | r \rangle \langle r |$,

b) bicentric $\delta\beta_{rs}(| r \rangle \langle s | + | s \rangle \langle r |)$.

The first-order, viz. second order corrections to the energy are:

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a) $E^{(1)} = \delta\alpha_r$,

$$E^{(2)} = (\delta\alpha_r)^2/[4\beta(\sqrt{3} - F_r)];$$

b) e.g. when both r and s belong to the same molecule and are both starred

$$E^{(1)} = 0,$$

$$E^{(2)} = (\delta\beta_{rs})^2/[\beta(2\sqrt{3} - F_r - F_s)].$$

The convergence of the perturbation series can be judged by the example of the pyridine molecule; with $\delta\alpha_r = 0.5\beta$, the following results are obtained, by using the ALMO's of benzene:

- variational energy (see e.g. [15, 16]): $6\alpha + 8.55\beta$;
- perturbational contributions:

$$E^{(0)} = 6\alpha + 8.00\beta, \quad E^{(1)} = 6\alpha + 0.50\beta,$$
$$E^{(2)} = 6\alpha + 0.05\beta.$$

Similar results are obtained by perturbing cyclodecapentaene to azulene ($\delta\beta_{15} = 1.\beta$):

- variational (see e.g. [15, 16]): $10\alpha + 13.36\beta$;
- perturbational:

$$E^{(0)} = 10\alpha + 12.94\beta, \quad E^{(1)} = 0,$$
$$E^{(2)} = 10\alpha + 0.39\beta,$$

resulting a value $E = 10\alpha + 13.33\beta$. We notice that for benzene and cyclodecapentaene free valence can be calculated from the formula for cyclic polyenes [15]:

$$F_r = \sqrt{3} - (4/n)\operatorname{cosec}(\pi/n),$$

n being the number of C-atoms in the polyene.

The values obtained here are also close to those obtained by the usual perturbation theory formulas (see e.g. [15, 16]): $E^{(1)}$'s are identical with those issued from our perturbation treatment, $E^{(2)}$ is 0.05β for pyridine and 0.44β for azulene. Third order terms can be included in our treatment, as they are very simple. By using variational perturbation formulas [13] the energy value can be further improved (e.g. for azulene $E = 10\alpha + 13.35\beta$).

ALMO's are suitable for qualitative discussions, in which case graphical methods can be helpful [17].

The perturbation effects increase with the decrease of the difference between the virtual and occupied ALMO energies. This explains the observed correlation between the free valence and the localization energy, as well as the importance of the former in chemical reactivity [18].

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