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QUASI-ONE-DIMENSIONAL APPROXIMATION IN THE HMO MODEL OF POLYMETHINE DYES

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In the framework of the Hueckel molecular orbital (HMO) model, an analytical method has been elaborated which enables calculation of energy levels and wave functions for polymethine dye molecules with arbitrary end groups characterized by two effective additive parameters. The method represents a generalization of the known long-chain approximation (LCA) manipulating only frontier π-MOs and yields analytical relations for molecular characteristics based on all occupied dye π-MOs.

Keywords: polymethine compounds, long-chain approximation, quasi-one-dimensional approximation, Green's functions, atomic charges, bond orders

In spite of the fact that the HMO approximation does not account for interelectronic interactions explicitly, the theory of polymethine dyes is greatly indebted to it, as this model affords a qualitative insight into the effects caused on the chemical and optical behavior of a dye Γ_1-$(CH)_x$-Γ_2 by its end groups Γ_1 and Γ_2 [1]. On the other hand, the HMO method, as such, is not adequate for the analytical treatment of the structure-property relationships. however simplistic this approach is, it offers only numerical potentialities for finding the energy

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spectrum and molecular wave functions. In a search for an appropriate toolkit which would enable one to establish analytical relationships between the integral properties of a dye molecule and its end-group characteristics, a number of approximations have been developed, as for instance, Dewar's perturbation theory [2,3] or the long-chain approximation (LCA) [4-6].

The latter implies that the polymethine chain consisting of N methine units is long enough, so that the frontier energy levels lie very close to the Fermi level, at a small energy distance of the order $(N+1+L)^{-1}$, and the frontier MOs are found by expanding the corresponding Hueckel-based expressions in this small parameter. The quantity $L = L_1 + L_2$ entering in it is the sum of the effective lengths of the end fragments; they are easy to calculate for an arbitrary specific end group, as also are other significant additive end-group parameters, electron donor abilities [5,6]. As the energy levels of the frontier MOs exert a paramount influence on the wavelength of the first electron transition and the reactivity of a dye (in terms of its donor-acceptor properties), these all- important characteristics prove to be expressed, in a very straightforward manner, in terms of the additive effective end-group parameters.

Besides the properties governed by the frontier MOs, there exist a number of essential molecular characteristics which cannot be derived without the knowledge on the entire energy spectrum of the system concerned. Among them are atomic charges and bond orders [1], linear and nonlinear electronic polarizabilities [7,8] etc. (The treatment of the polarizabilities in the framework of LCA was restricted to the two-level model) [9]. In the present study, we generalize LCA so as to calculate not only frontier MOs but also all the MOs mainly localized on the polymethine chain (i.e. excluding those localized completely on the end groups). For a sufficiently long polymethine chain, it is these MOs that dictate the properties manifested by a dye.

Unlike LCA, the supposed approach implies that Green's functions of end groups are approximated by their "quasi-one-dimensional" analogues (i.e., Green's functions referring to periodic chains). Accordingly, the new approximation is called quasi-one-dimensional. As is shown later, it reduces to a particular case, LCA, as far as frontier MOs are concerned, exactly reproduces the HMO-based spectrum for some specific dye systems, and describes, to a sufficient accuracy, the quasi-continuous picture of a real spectrum in the general case. The applications of the approach elaborated will be exemplified by the analytical expressions for the

alternating contributions to π-atomic charges and π-bond orders within the polymethine chain with arbitrary end groups.

To derive the quasi-one-dimensional approximation, we make use of the representation of the exact HMO method formulated in the form which refers to the spectrum z_q and the wave function $\Psi_n(q)$ of the unsubstituted chain [6]:

$$z_q = -2\cos\theta_q, \quad \theta_q = \frac{\pi\left[q + f(\theta_q)\right]}{N+1} \tag{1}$$

$$\Psi_n(q) = \sqrt{\frac{2}{N+1-\pi f'(\theta_q)}}\sin\left[\theta_q n - \pi f_1(\theta_q)\right] \tag{2}$$

$$f(\theta_q) = \sum_{j=1}^{2} f_j(\theta_q), \quad f_j(\theta) = \frac{1}{\pi}\operatorname{arccot}\frac{1+\beta_{jC}^2 g_j(\theta)\cos\theta}{\beta_{jC}^2 g_j(\theta)\sin\theta} \tag{3}$$

$$g_j(\theta) = \langle\tilde{j}|(z-\hat{H}_j)^{-1}|\tilde{j}\rangle \tag{4}$$

Here the Coulomb integral of the carbon atom, α_C, is put equal to zero, and the absolute magnitude of the resonance integral for a bond between the neighboring carbon atoms, $|\beta_{CC}|$, is taken equal to unity so that the energy spectrum of a dye, z_q, and the resonance integrals for the bonds adjacent to end groups, β_{jC}, are measured in units $|\beta_{CC}|$. For an unsubstituted chain, we have $f_j(\theta_q) \equiv 0$ and the Eqs. (1) and (2) reduce to simple analytical dependences on the level number $q = 1, 2, \ldots, N$. The end groups are characterized by the Hamiltonians $\hat{H}_j$ written as in the exact HMO method and by Green's functions (4) calculated for the end groups at the atoms which are bound to atoms 1 and N of the polymethine chain and designated by $\tilde{j}$. Functions $f_j(\theta_q)$ specified by Eq. (3) and determined by corresponding Green's functions enter in Eq. (1) for the variable θ_q. The family of solutions of this transcendent equation furnishes the energy spectrum z_q and the wave function $\Psi_n(q)$ specified by Eq. (2), just as would be the case if the eigenvalues and eigenfunctions of the Hueckel Hamiltonian were found.

The quasi-one-dimensional approximation consists in the linearization of the function $f_j(\theta)$:

$$f_j(\theta) = \varphi_j - \frac{1}{\pi} l_j \theta , \tag{5}$$

which enables determination of the energy spectrum and the wave function in a very straightforward way:

$$\theta_q = \frac{\pi(q+\varphi)}{N+1+l}, \quad \varphi = \sum_{j=1}^{2} \varphi_j , \quad l = \sum_{j=1}^{2} l_j , \tag{6}$$

$$\Psi_n(q) = \sqrt{\frac{2}{N+1+l}} \sin\left[\theta_q (n + l_1) - \pi \varphi_1\right] \tag{7}$$

Physically, the linearization specified by the above relation implies that real Green's function (4) is substituted by the approximate expression

$$\beta_j^2 g_j(\theta) = -\cos\theta + \sin\theta \cot\left[(l_j + 1)\theta - \pi \varphi_j\right], \tag{8}$$

which results from equating relations (3) and (5). Such a cotangential behavior of Green's function is inherent in quasi-one-dimensional systems of locally attached fragments [5]. As a particular case, at $\varphi_j = 0$ and with an integer l_j formula (8) yields Green's function for a chain of identical atoms (the end fragment j is represented by the polymethine chain). That is why, the linearization performed by Eq (5) is exact in this situation. It is likewise exact for the end groups represented by heteroatoms with $\beta_{jC}^2 = 1$ and $\alpha_j = \pm 1$, as is the case for nitrogen and boron atoms). Indeed, substituting of Green's function for a heteroatom, $g_j(\theta) = -(2\cos\theta + \alpha_j)^{-1}$, in Eq (3) leads to a linear dependence in Eq. (5) at $\alpha_j = 0$ (a trivial instance when the polymethine chain is lengthened by a single methine unit) and at $\alpha_j = \pm 1$ For the latter case, the parameters φ_j and l_j take on the following values: $\varphi_j = l_j = 1/2$ for a nitrogen atom ($\alpha_j = -1$) and $\varphi_j = 1$, $l_j = 1/2$ for a boron atom ($\alpha_j = 1$).

To illustrate the accuracy of the linearization afforded by Eq. (5), compare the exact (HMO-provided) and approximately calculated (by the model proposed) dependences $f_j(\theta)$ for the end atom with the parameters $\alpha_j = -1/2$ and $\beta_{jC}^2 = 1/2$ (see curves 1 and 2 in Fig. 1). These values of the atomic parameters determine the effective end-group (end-atom) parameters $\varphi_j = 1$, $l_j = 3/2$ (the linearization coefficients in Eq. (5)). As seen from Fig. 1, the approximate linear dependence specified by Eq. (5) is tangential to the exact function at the central point $\theta = \pi/2$ corresponding to the position of the Fermi level of the dye molecule. Therefore, the approximation is particularly efficient in the vicinity of this significant peculiar point (it is just in this region that the LCA operating on the frontier MOs is applicable adequately). The distinctions in the dependences plotted which become rather material near the interval boundaries (0 and π) are attributable to the contributions from the MOs localized on the end groups, since they are not considered within the approximation concerned.

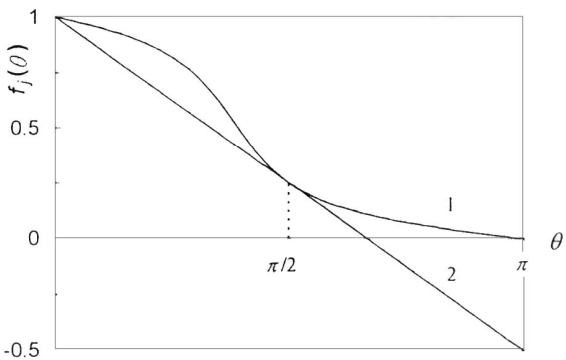

Fig. 1. The dependence $f_j(\theta)$ based on the exact HMO method (curve 1) and approximated by Eq. (5) (curve 2) for the end atom with the parameters $\alpha_j = -1/2$ and $\beta_{jC}^2 = 1/2$.

We now turn to the reducibility of the quasi-one-dimensional approximation to LCA. The latter suffices in the vicinity of $\theta = \pi/2$. The electron donor ability F_j is given by the value $f_j(\theta)$ at $\theta = \pi/2$:

$$F_j = f_j(\pi/2) = \varphi_j - l_j/2, \tag{9}$$

and the effective length L_j coincides with the linearization coefficient l_j in Eq. (5). Most typically, LCA manipulates polymethine chains containing odd numbers N of methine groups. Then the values of the positive and negative energy levels closest to zero (LUMO and HOMO, respectively) are defined by the values $q = (N+1)/2$ and $q = (N-1)/2$. Substitution of relation (9) into Eqs. (1), (6), and (7) yields the LUMO value:

$$z_{\mathrm{LUMO}} = 2\sin\frac{\pi F}{N+1+L} \approx \frac{2\pi F}{N+1+L} \tag{10}$$

$$\Psi_n(\mathrm{LUMO}) = \sqrt{\frac{2}{N+1+L}}\sin\left[\frac{\pi}{2}n + \frac{\pi F}{N+1+L}(n+L_1) - \pi F_1\right] \tag{11}$$

The corresponding expressions for HOMO result from relations (10) and (11) by replacing F - 1 for F. Relations (10) and (11) just represent the pivotal outcomes of LCA [6]. (A small term containing L_1 in Eq. (11) which provides the wave function symmetry with respect to the end group interchange was neglected before). The approximate equality in relation (10) holds due to the smallness of the quantity $(N+1+L)^{-1}$. Formula (10) elucidates the physical meaning of the electron donor ability F (varying from 0 to 1): this parameter characterizes the HOMO and LUMO positions relative to the Fermi level. The reciprocal of the gap between the two frontier MOs gives the wavelength of the first electronic transition and proves to be proportional to the factor $(N+1+L)$.

Comparing to LCA, the quasi-one-dimensional approximation determined by Eqs. (6) and (7) has the advantage that it enables determination of various molecular characteristics contributed by all occupied MOs. Owing to the simple form of wave function (7), the MO contributions can be summed so that the result is expressible analytically. To exemplify this statement, we present the formulae of the quasi-one-dimensional approximation which

determine the alternating contributions to atomic charges, $\rho_n^{(\mathrm{alt})}$, and bond orders, $b_n^{(\mathrm{alt})}$ (nonalternating contributions to these quantities arise from the MOs localized on end groups and hence being beyond the limits of present approximation).

$$\rho_n^{(\mathrm{alt})} = (-1)^n \frac{\sin\left[2\pi F_1 - 2\pi F(n+L_1)/(N+1+L)\right]}{(N+1+L)\sin\left[\pi F(n+L_1)/(N+1+L)\right]} \tag{12}$$

$$b_n^{(\mathrm{alt})} = (-1)^{n+1} \frac{\cos\left[2\pi F_1 - 2\pi F(n+L_1+1/2)/(N+1+L)\right]}{(N+1+L)\sin\left[\pi F(n+L_1+1/2)/(N+1+L)\right]} \tag{13}$$

The above relationships are valid for even N. Their counterparts for odd N are obtainable from Eqs. (12) and (13) by the substitution of $F - 1/2$ for F. The comparison with the results provided by the exact HMO method evidences for a high accuracy of the quasi-one-dimensional approximation for a variety of end groups [10].

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