"Configuration Analysis" in the LCAO-MO Method

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The semiempirical LCAO-SCF-MO method including CI, developed by Pariser, Parr and Pople, has been applied to a number of molecules by the aid of electronic computers. One of the disadvantages of this method is that the wave functions calculated for molecular electronic states are often hardly understandable, which fact originates from the nature of the SCF-MO's themselves. Only a few attempts have been made to improve this situation in rather limited cases.[1,2] In this communication we propose a procedure which leads in an easy and unambiguous way to a useful interpretation of the wave functions concerned.

Let n AO's χ_p be represented by a row vector $\boldsymbol{\chi}$, and the n SCF-MO's ϕ_i by $\boldsymbol{\phi}$; the latter can be written as $\boldsymbol{\phi}=\boldsymbol{\chi}\mathbf{C}$ where $\mathbf{C}$ is an n-dimensional square matrix. Suppose that $\boldsymbol{\phi}^0$ represents a set of n orthonormal MO's $\phi_i{}^0$ which are expressed as linear combinations of the χ's, that is, $\boldsymbol{\phi}^0=\boldsymbol{\chi}\mathbf{C}^0$. Then it follows that $\boldsymbol{\phi}=\boldsymbol{\phi}^0\mathbf{B}$ with $\mathbf{B}=(\mathbf{C}^0)^{-1}\mathbf{C}$. Collect $2n$ MSO's λ_ξ in $\boldsymbol{\lambda}=(\lambda_1\lambda_2\cdots\lambda_{2n})=(\phi_1\alpha\,\phi_2\alpha\cdots\phi_n\alpha\phi_1\beta\phi_2\beta\cdots\phi_n\beta)$, and similarly MSO's $\lambda_\xi{}^0$ in $\boldsymbol{\lambda}^0$. It can then be shown that $\boldsymbol{\lambda}=\boldsymbol{\lambda}^0\mathbf{A}$ with $\mathbf{A}=\mathbf{E}\times\mathbf{B}$, where $\mathbf{E}$ is the two-dimensional unit matrix. Let the number of electrons concerned be denoted by N. It is now verified that a Slater determinant $\Phi[\lambda_{\xi_1}\lambda_{\xi_2}\cdots\lambda_{\xi_N}]$ can be expanded in terms of Slater determinants built from λ^0's. Thus one obtains

$$\Phi[\lambda_{\xi_1}\lambda_{\xi_2}\cdots\lambda_{\xi_N}] = \sum_{(\eta_1,\eta_2,\cdots,\eta_N)} \Phi^0[\lambda_{\eta_1}{}^0\lambda_{\eta_2}{}^0\cdots\lambda_{\eta_N}{}^0] \times \begin{vmatrix} a_{\eta_1\xi_1} & a_{\eta_1\xi_2}\cdots a_{\eta_1\xi_N} \\ a_{\eta_2\xi_1} & a_{\eta_2\xi_2}\cdots a_{\eta_2\xi_N} \\ \cdots\cdots & \cdots\cdots\cdots\cdots \\ a_{\eta_N\xi_1} & a_{\eta_N\xi_2}\cdots a_{\eta_N\xi_N} \end{vmatrix} \tag{1}$$

where $(\eta_1, \eta_2,\cdots,\eta_N)$ is a combination of $2n$ integers $1, 2,\cdots,2n$ taken N integers at a time, and the $a_{\eta\xi}$'s are the elements of the matrix $\mathbf{A}$.

By the use of Eq. (1) the wave function, V (or T), for any singlet (or triplet) configuration constructed from the SCF-MO's ϕ_i can be expanded in terms of V^0's (or T^0's), the latter being singlet (or triplet) configurational wave functions constructed from the MO's $\phi_i{}^0$. For instance, the ground configuration V_0 and a singly excited configuration V_{IK} are shown to be expanded as follows:

$$V_0 = D_0{}^2V_0{}^0 + \sum_{i=1}^{m}\sum_{k=m+1}^{n}\sqrt{2}\,D_0D_{ik}V_{ik}{}^0 + \cdots$$

$$V_{IK} = \sqrt{2}\,D_0D_{I'K'}V_0{}^0$$

$$\sum_{i=1}^{m}\sum_{k=m+1}^{n}(D_0D_{ik,I'K'} + D_{ik}D_{I'K'})V_{ik}{}^0 + \cdots$$

where $m=N/2$. D_0 is the determinant formed from the first m rows and the first m columns of the matrix $\mathbf{B}$, and $D_{ik,I'K'}$ is the determinant formed from the same rows and columns of the matrix which is obtained from $\mathbf{B}$ by replacing its ith row and Ith column by its kth row and Kth column, respectively.

With aniline, for instance, one may choose the benzene MO's and the nitrogen 2pπ AO for $\phi_i{}^0$. Then $V_{ik}{}^0$ should correspond to locally excited configurations or charge-transfer configurations. With pyridine one may conveniently use the benzene-like MO's as $\phi_i{}^0$.

By choosing suitable MO's for $\phi_i{}^0$ in the above way, V's (or T's) can be analyzed into the configurations V^0's (or T^0's) which can be easily understood from a physical or chemical viewpoint. In this sense, the present procedure will be called "configuration analysis." The details of the procedure together with its applications to various types of molecules will be published later.

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