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Studies on the Electronic Structure of Conjugated Systems*

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A comprehensive study of the electronic structure of conjugated systems, within the π approximation and using a CI SCF procedure, has been undertaken. In this work the common features (method and approximations, semiempirical parameters, details of the program, etc.) are examined and the general characteristics of the results are discussed.

Eine ausführliche Untersuchung der Elektronenstruktur konjugierter Systeme wurde mit Hilfe eines CI SCF Verfahrens innerhalb der normalen π-Annäherung durchgeführt. In der vorliegenden Arbeit werden die Grundzüge (wie Methode und Näherungsverfahren, halbempirische Parameter, Einzelheiten des Programms, usw.) besprochen.

On a entrepris une étude compréhensive de la structure électronique des systèmes conjugués, dans le cadre de l'approximation π et en utilissant la méthode de champ auto-cohérent avec interaction de configurations. Dans le présent travail on éxamine les charactéristiques générales (méthode et approximations, paramètres sémiempiriques, détails du programme, etc.).

Introduction

Since the original treatments of Hückel [7], Goeppert-Mayer and Sklar [4], Pariser and Parr [8, 9], and Pople [10], calculations on conjugated systems have enjoyed a wide popularity, leading to a wealth of theoretical results. The efforts, however, have been directed generally towards the development of criteria, on the basis of a comparison with experimental data, on which to judge the validity of general methods and specific approximations and to decide the choice of the semiempirical parameters to be used, with the result that so far very few extensive studies have been carried out in a systematic manner. Only the Hückel calculations of Streitwieser and Brauman [13], Coulson and Streitwieser [1], and Heilbronner and Straub [5] can be included in this category; there are, however, no comparable compilations at a higher level of sophistication, although some series of systems have been studied recently.

As new generations of computers come into use, the time problem is being overcome and more sophisticated calculations are now possible. Improvements in the methods avoid the necessity of having to tinker with the input parameters, and an economic mass production of satisfactory data is feasible.

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In this general project, a comprehensive study of numerous systems has been undertaken, using a standard set of input data and carrying out the calculations within the framework of the self-consistent field (SCF) method with configuration interaction (CI).

Details of the Calculations

Theoretical Formulation

The calculations have been restricted to systems with closed-shell configurations in the groundstate. The CI treatment has been carried out using the occupied and virtual orbitals obtained by the Roothaan [11] SCF procedure for the groundstate.

The matrix elements of the Hartree-Fock operator in the single-configuration treatment have been defined as

$$F_{uu} = -\alpha'_{uu} + D_{uu}J_{uu} + \sum_{v \neq u} (2D_{vv} - n_v) J_{uv} ,$$

$$F_{uv} = \beta_{uv} - D_{uv}J_{uv} ,$$

with

$$\alpha'_{uu} = W_u + (n_u - 1) J_{uu} ,$$

$$D_{uu} = \sum_i c_{ui}^2 .$$

W_u denotes the ionization potential (in absolute value) of a π electron in atom u in the corresponding valence state, c_{ui} represents the expansion coefficient for the $2p$ orbital on atom u in the i-th molecular orbital, and n_u is the number of π electrons contributed by atom u. J_{uv} is the two-electron coulomb integral between the $2p$ orbitals centered on atoms u and v. The summation over v extends over the centers in the system while the summation over i runs over all the occupied orbitals.

The one-electron (kinetic and nuclear attraction energy) terms have been approximated by

$$\alpha_{uu} = -\alpha'_{uu} - \sum_{v \neq u} n_v J_{uv} ,$$

$$\beta_{uv} = \tfrac{1}{2} S_{uv} (F_{uu} + F_{vv}) ,$$

where S_{uv} denotes the overlap integral between the $2p$ orbitals on atoms u and v.

In the many-configuration approximation only those configurations, considered by Fraga and Ransil [2], arising from single and double excitations, have been included. (Denoting by i, j and a, b the occupied and virtual orbitals, respectively, the excitations considered may be represented by $(i)^2 \to (a)^2$, $(i)(j) \to (a)^2$, $(i)^2 \to (a)(b)$, and $(i) \to (a)$. The corresponding number of configurations depends on the available occupied and virtual orbitals; in the present calculations a maximum of fifty-five configurations, involving three occupied and four unoccupied orbitals, or vice versa, have been included, whenever possible.) The corresponding elements of the interaction matrix have been evaluated using the formulas of Fraga and Ransil [2].

Integrals and Parameters

The integrals S_{uv}, J_{uv} have been evaluated using the formulation of Roothaan [12], with orbital exponents chosen in order to fit the one-center coulomb integrals, J_{uu}, that have been approximated by

$$J_{uu} = W_u - A_u \,,$$

where A_u denotes the electron affinity (in absolute value) of atom u in the corresponding valence state.

The values for W_u and A_u have been taken from, or derived from the data of Hinze and Jaffe [6]. (The Hartree-Fock values of Thorhallsson, Fisk, and Fraga [14] would lead to very similar results).

Bond Distances and Angles

The experimental values for the bond lengths, whenever available, have been used in the calculations, but it should be mentioned that for crystalline systems averages of the experimental values for chemically equivalent bonds have been taken. For those systems for which no experimental data were available, the corresponding bond lengths have been estimated from the known values for similar systems. In the calculations, the deviations from the chosen bond lengths have been of the order of ± 0.02 Å, due to the fact that the coordinates and not the bond lengths are used as input data.

Regarding the bond angles, values of 120° have been taken in open chains and homocyclic hexagonal molecules, with corrections for the latter of up to ± 4°, in order to accommodate systems with different bond lengths. In the case of hexagonal heterocycles with N, the angles CCC have always been taken slightly larger than the angles CNC; and for non-hexagonal cyclic systems angles very close to those in the corresponding regular polygon have been used.

The accuracy of the input data for the coordinates has been tested on the basis of the symmetry characteristic of the results.

Results and Discussion

The calculations yield the following results:

a) single-configuration approximation: expansion coefficients; orbital energies; electronic and total energies and effective charges for the negative ion, groundstate and first triplet and singlet excited states of the neutral system, and positive ion; and the bond orders for the groundstate of the neutral system.

b) many-configuration approximation: electronic energies, before and after CI, of all the excited states considered; expansion coefficients and dipole oscillator strengths for those excited states lying below the positive ion; and effective charges and bond orders for the groundstate of the neutral system.

The calculations have been carried out for 613 systems, including: polyenes; phenyl-polyenes; diphenyl-polyenes; cata-condensed hydrocarbons; peri-condensed hydrocarbons (consisting only of six-membered rings and of six- and five-membered rings); hydrocarbons derived from biphenyl; azaderivatives of benzene, naphthalene, anthracene, and phenanthrene; heterocycles with one, two, and three heteroatoms in a five-membered ring and their derivatives; dihydrodiazines, oxazines, dioxines, and some of their derivatives; aza-azulenes; heterocycles with one and three heteroatoms in a seven-membered ring and some of their derivatives; hydroxy-derivatives of naphthalene, anthracene, phenanthrene, and other systems; aldehydes of polyenes, phenyl-polyenes, cata- and peri-condensed hydrocarbons; ketones; quinones; amino- and hydroxy-amino-derivatives of naphthalene, anthracene, phenanthrene, pyrene, perylene, fluoranthene, and other systems; derivatives of benzene; and derivatives of pyridine, quinoline, isoquinoline, tricyclic systems with N, and heterocycles with O.

A meaningful discussion of the present results should include an exhaustive comparison with existing theoretical values and experimental data. Due to the wealth of results obtained, it is clear that they cannot be presented here[1]. Consequently only some general comments, regarding the characteristics of the results, will be made here.

Two points require special mention. On one hand it is believed that the predictive value of the present calculations is comparable (with due consideration to the approximations involved) to that of the minimal basis set calculations carried out for small molecules. On the other hand they can be considered as *a priori* calculations, due to the fact that standard parameters are used, with no parametrization introduced at all. For these reasons it is hoped that the present results may serve as a point of reference for more sophisticated treatments.

Regarding the separate quantities evaluated one can summarize some of the results (on the basis of the overall behavior and by comparison with experimental values, where pertinent and available) in the following way. Configuration interaction leads to a very small lowering of the energy of the groundstate (as it has consistently been reported in the literature), but on the other hand a satisfactory overall prediction of the electronic spectra is made, especially insofar as the main transitions are concerned; the results are better, of course, for those systems with less symmetry, where a larger number of configurations is actually involved in the CI treatment of each symmetry. The orbital energies calculated may be taken, as a whole, to give a good prediction of ionization potentials, but on the other hand it would seem that the virtual orbital approximation does not provide a satisfactory prediction of electron affinites, although the inclusion of an additive term (within a given series of related systems) would correct such a situation. It must be mentioned also that, in general, it seems that if only the electronic density distribution were needed, it would be sufficient to carry out a simple Hückel calculation, a fact already pointed out by Fraga and Valdemoro [3].

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[1] The complete results have been collected in the Technical Reports TC-6901, TC-6902, TC-6903, TC-6905, TC-6907, TC-6909, TC-6911, TC-6913, TC-6915, TC-6917, and TC-6919, Department of Chemistry, University of Alberta (1969). These Reports have been placed at the National Science Library, National Research Council, Ottawa 7, Ontario, Canada. In addition, a limited number of copies are available from the authors upon request.

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