Theoret. chim. Acta (Berl.) 10, 247—253 (1968)

Further Studies on Configuration Interaction in the Molecular Orbital Theory of π-Systems

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Received January 10, 1968

The effect of triply-excited configurations on the calculated energies for sixteen electronic transitions in eleven unsaturated hydrocarbons has been investigated. The spectra were calculated using a Pariser-Parr-Pople approach modified by a variable electronegativity self-consistent field treatment. The agreement with experiment is improved, but not as dramatically as expected. The implications of these results for other types of semi-empirical calculations are discussed.

Die Auswirkung des Einschlusses dreifach angeregter Konfigurationen auf 16 Übergangsenergien von 11 ungesättigten Verbindungen ist untersucht worden, wobei nach einem SCF-PPP-Formalismus mit variabler Elektronegativität vorgegangen wurde. Die Übereinstimmung mit dem Experiment ist nur wenig besser, so daß meist keine Notwendigkeit besteht, Anregungen des obigen Typs in die Rechnung einzuschließen.

Etude de l'effet des configurations triexcitées sur les énergies calculées pour seize transitions électroniques dans onze hydrocarbures non saturés. Les spectres ont été calculés en utilisant une méthode de type Pariser-Parr-Pople modifiée par un traitement self-consistant à électronégativité variable. L'accord avec l'expérience est amélioré, mais d'une manière moins dramatique que prévu. On discute les conséquences de ces résultats pour d'autres types de calculs semi-empiriques.

Introduction

The calculation of the properties of those molecules amenable to a π-electron treatment has received considerable attention during the last few years. By far the major portion of this effort has, somewhat regretably, been directed towards the inclusion of new types of molecules. The list of compounds for which inaccurate predictions of physical properties are now available is quite impressive.

A reexamination of the methods employed for semi-empirical calculations was probably first called for by Coulson [1] in a 1959 conference, and the pleas have been renewed by Parr [2] and most recently by Pople [3]. At the Istanbul Lectures [4], Parr listed a decade of problems in this domain, which still remain unresolved. Varying amounts of work are being done in each of the areas suggested, but one of his questions overshadowed the others for us: "How much configuration interaction?"

Many investigators have touched on this problem, as have we [5, 6], but generally the conclusion has been that the extent of configuration interaction (CI) necessary or desirable was the amount that the researcher was capable of performing without too much effort or inconvenience. We have recently reviewed the publications on this topic [6].

The one conspicuous exception to this general state of affairs – the only attempt to really tackle the question – is the group of papers by Koutecký and coworkers [7, 8, 9]. We find these studies most important, for they both complement and amplify our work. These papers consider only the benzene molecule.

Using several different sets of parameters from the literature, both theoretical and semi-empirical, the energies of the ground and excited states resulting from an interaction treatment were calculated. They started with all the singly-excited configurations, and then extended it to a doubly-, a triply-, and finally a complete sextuply-excited CI. The results that are important for our considerations here may be summarized as follows:

1. Doubly-excited configurations have a considerable effect (up to 2 eV) upon the transition energies.
2. The effect of triply-excited configurations is considerably less – a few tenths of an electron volt at most (but still substantially greater than the errors usually encountered in an experimental determination).
3. The addition of the remainder of the multiply excited configurations had a negligible (of the order of hundredths of an electron volt) effect upon the transition energies.

These general conclusions apply to the cases of parameter sets for which a minimal extent of CI was necessary, including the Pariser-Parr-Pople type of approach [10–12] which we employ. The general conclusions are somewhat discouraging, for one cannot at present hope to include in a calculation all of the configurations up through triply-excited for molecules much larger than benzene.

We began our studies before the appearance of Koutecký's work, but, anticipating the results of such an approach, we posed the question somewhat differently. How high an energy, we asked, must a configuration possess before there is no effect upon the predicted transition energy? We have recently published our initial answers to this problem [6], and conclude our studies here.

Our initial findings were based upon a study of three molecules, *1,3,5,7*-octatetraene, styrene and naphthalene. We chose these eight- and ten π-electron systems because they were large enough to reflect the problems inherent in still larger systems, small enough to allow the consideration of configurational energy levels beyond the point of influence on the predicted transitions, and diverse enough in structure to be generally representative of π-systems. Working only with the doubly-excited configurations we concluded that if one desires an accuracy of no more than 0.1–0.2 eV (compared with that of a complete CI treatment), then:

1. It is not necessary to include all of the doubly-excited configurations.
2. It may be highly desirable to include some triply-excited configurations.
3. The cut-off point is at approximately 20 eV above the ground configuration.

On the basis of these conclusions, the next logical step is to show the extent to which triply-excited configurations do in fact influence the outcome of a Pariser-Parr-Pople type of calculation. We have made several modifications of the basic approach [5, 13, 14], the most important of which is the use of the variable electronegativity self-consistent field procedure of Brown and Heffernan [15] including an allowance for the inductive effect of substituent groups. However, the particular method used here is of little consequence in so far as the conclusions which we draw, for, as shown by Koutecký's papers, they may be applied to any semi-empirical calculation of the general Pariser-Parr-Pople type.

We shall here select several unsaturated hydrocarbons, calculate their ultraviolet spectra including only singly- and doubly-excited configurations, then add triply-excited wave functions, and finally compare the results obtained with the two approaches.

Methods of Calculation

It is a much more formidable problem to calculate a configuration interaction (CI) matrix with triply-excited configurations than might at first be expected. From a doubly- to a triply-excited treatment, the number of distinct wave functions is only increased by ten, but the number of interactions is enormous. In the case of naphthalene the change is from 140,000 to more than two million. Though a large portion of elements in both cases is zero (due to either a forbidden nature or symmetry requirements) there are still many elements remaining.

The usual procedure employed when one wishes to calculate the energy levels for such molecules is to develop the spin-free expressions for each interaction element. Many of the elements possess expressions of the same form, perhaps differing only as to the signs of the component terms of repulsion integrals. It is then not too difficult to design a program which will iterate over the configurations and interaction elements, employ the integrals appropriate to a particular molecule, and finally choose the correct signs and expressions. It is not an impossible task for doubly-excited configurations, but the debugging of such a program is a long and tedious problem. We decided that the programming of such a method of calculation for a triply-excited CI matrix would probably require several man-lives.

The most straightforward approach is, of course, that used when it is desirable to calculate the properties of a single molecule. One simply starts with the spin-dependent wave functions and calculates each element. Though this is not at all difficult for a small molecule by hand, it would require a relatively sophisticated program in order to treat any unsaturated system. This type of calculation possesses a strong advantage in that it will reach an error-free condition with little effort. However, it also requires an enormous amount of running time for a molecule of appreciable size. We chose the first mentioned method for doubly-excited configurations for just this reason, and it would be quite impractical to employ the straight-forward approach for triply-excited configurations.

We took an intermediate path. Beginning with the wave functions for each excited configuration, the spin-independent expressions for every possible interaction between a triply- and any singly-, doubly-, or triply-excited configuration were calculated. All the allowed elements were then stored on tape. They were ordered in such a way that all the interactions with any particular configuration were grouped together. Thus, in the calculation of a row of the CI matrix, the appropriate of expressions were all in the core memory. Though the extensive duplication in the calculation of sums of molecular core and repulsion integrals required approximately 60 hours of 7074 time, this direct approach resulted in a concise fast-running program devoid of logic concerning signs, and simple to debug. No molecule reported here necessitated more than about two minutes for the construction of the CI matrix.

For this study of the effect of a triply-excited CI treatment we have chosen eleven compounds with sixteen transitions. These unsaturated hydrocarbons were used for the comparison with the doubly-excited treatment previously described [14] for two reasons. First, the spectra of these compounds were among the most accurately and completely recorded available. More often than not, only the position of maximum intensity is reported in the literature for a transition, and one cannot be at all sure this is close to the center of the integrated absorption intensity. Several polyenes reported earlier were not included since (as noted there) the configurations are ambiguous: *s-cis* or *s-trans*. Then, too, in some cases there is the possibility that absorption does not represent a $\pi \rightarrow \pi^*$ transition [14]. We felt that the chosen compounds avoided all these difficulties, and were reasonably pure.

The second reason was dictated by our program. Naphthalene and azulene, among all the other compounds studied in the previous work, would also meet the above criteria. However, we have not yet incorporated a routine for deciding which interactions to calculate (based upon the 20 eV cut-off described above). Without this, the running time would have been too long for these systems.

However, a preliminary calculation of the spectrum of cyclooctatetraene was performed. With the reference resonance integral set at a slightly higher value than that eventually employed (see below), the transition shifted 0.20 eV from 5.48 eV with a doubly-excited CI treatment to 5.28 eV when all doubly- and triply-excited configurations (436) up to 24 eV were included. This is, nevertheless, still considerably greater than the experimental value (4.4 eV, although the maximum in the absorption band cannot be accurately located [14]). There would probably be a slight shift (in the wrong direction) for the empirical integrals which gave the best overall fit, but it was not calculated because the running time for this compound is several hours on the IBM 7074. In any case it could not be included in the Table since it does not meet the criteria noted above.

Though the CI matrices for the compounds listed in the Table were not truncated to 20 eV since they could be easily handled, it is expected that such a truncation would have no important effect on the results.

The method of calculation is identical to that reported for the doubly-excited CI treatment, except for the numerical value of the resonance integral. The procedure is detailed in Ref. [14]. The core integrals (β) for nearest neighbors are calculated from the Mulliken formula:

$$\beta_{pq} = -A \cdot S_{pq}(W_p + W_q)/2(1 + S_{pq}),$$

where A is determined by the empirically chosen reference set of resonance, overlap (S) and ionization integrals [5]. In the above equation the quantity $S_{pq}/(1 + S_{pq})$ is replaced by an empirical expression for internuclear distances larger than those for nearest neighbors. Specifically, the following expression was employed when the overlap integral S was less than 0.14:

$$\beta_{pq} = -[A(W_p + W_q)/2]\ (44095\,S^5 - 15084\,S^4 + 1785\,S^3 - 804\,S^2 + 1.60\,S).$$

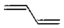
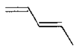
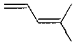
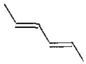
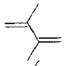
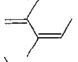
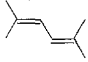
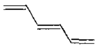
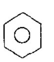
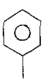
This expression allows β to fall off somewhat more rapidly as noted earlier [14]. The constant, A, was chosen to minimize the standard deviation between experimental and theoretical results. The change from the doubly-excited treatment is quite small: -1.220 eV here versus -1.186 eV when the configuration interaction was terminated at the doubly-excited stage. Since the value for A in the doubly-excited treatment carried out earlier was chosen to obtain the least error for a much larger basis set of alkenes, a check was made to determine that the same value would be the best fit for the doubly-excited treatment here, and it was.

Results and Discussion

As may be seen in the Table, the standard deviation between the predicted and experimental transitions has been improved by 0.04 eV – from 0.253 in the case of a doubly-excited treatment to 0.215 for a triply-excited CI. However, this is not the complete picture. For the worst transitions – all those which deviated from experiment by more than 0.3 eV for a doubly-excited CI calculation – the improvement is substantially larger; an average of 0.14 eV. This improvement is at the expense of the transitions which initially deviate less than 0.3 eV. Almost without exception, the agreement with experiment is slightly worse for each of these transitions. Since the group of transitions where the error was less than 0.3 eV were largely within experimental error of the observed values, either with or without the inclusion of the triply-excited configuration, the 0.04 eV improvement in the standard deviation is misleading.

The total effect of the triply-excited configurations on the energies of the transitions between the ground and singly-excited states is, however, somewhat smaller than we had anticipated. This may be seen more quantitatively in the

Table. *Effect of triply-excited CI on electronic transitions*[a]

Compound	Experimental Transition[b]	Doubly-Excited Configurations	Deviation from Exp.	Triply-Excited Configurations	Deviation from Exp.
1. 	5.92	5.91	−.01	5.95	+.03
2. 	5.78	5.77	−.01	5.81	+.03
3. 	5.54	5.63	+.09	5.67	+.13
4. 	5.60	5.65	+.05	5.69	+.09
5. 	5.64	5.79	+.15	5.83	+.19
6. 	5.44	5.65	+.21	5.69	+.25
7. 	5.20	5.44	+.24	5.48	+.28
8. 	4.96	5.21	+.25	5.27	+.31
	6.02	5.71	−.31	5.87	−.15
9. 	5.09	5.14	+.05	5.13	+.04
10. 	4.90	4.66	−.24	4.64	−.26
	6.19	5.76	−.43	5.84	−.35
	6.94	7.27	+.33	7.09	+.15
11. 	4.73	4.61	−.12	4.61	−.12
	6.08	5.69	−.39	5.78	−.30
	6.78	7.20	+.42	7.03	+.24
Standard Deviation			0.253 eV		0.215 eV

[a] All values in eV.

[b] See Ref. [14] for sources of these transitions.

coefficients of the final wave functions. The ground configuration is, of course, essentially unaffected, since there are no connecting elements with the triply-excited configurations. The singly-excited state wave functions contain from 1–5 % of all the triply-excited configurations. No single configuration was found to mix to an extent greater than 1 %. This is less than is usually observed for the mixing of doubly-excited configurations with the ground configuration, for which a total of a 10 % mixing is not unusual, though none of the molecules here reported exceed 7 %. It would be expected that the situation between singly- and triply-excited configurations would lead to larger rather than smaller effects, for the minimum separation between ground and doubly-excited configurations is generally 10–12 eV, whereas for the singly vs. triply case it can be almost as low as half this value. Of course, few of the many triply-excited configurations, it may be reasonably argued, lie low enough so that the analogy could be expected to hold strictly. On the other hand, it is often observed that a doubly-excited configuration of higher energy – within the range of the lower triply-excited configurations – will mix to the order of 10–20 or even 30 % with a singly-excited configuration. In fact, the mixing is not too uncommonly found to such an extent that one is hard-pressed to consider the resulting state as a singly-excited one.

Before one concludes that the improvement is considerably smaller than anticipated, however, there must also be an estimate of just how good a fit to the experimental data is to be reasonably expected. The compounds treated here were chosen in part because their spectra have been reproduced many times, and it would be unlikely that the band positions were in error by more than a few hundredths of an electron volt. But we are attempting to fit Frank-Condon bands, not the vibrational peaks, and this requires a subjective choice. It is difficult to believe that the standard deviation for such determinations could amount to less than 0.1 eV. With a larger basis set of compounds, where the structure, purity or spectral techniques may be dubious, our standard deviation of 0.21 eV is probably the best for which one could hope.

In summary, from the viewpoint of a 0.04 eV improvement, it would appear less than worthwhile for a worker involved in similar calculations to extend the CI treatment to triply-excited configurations, but the substantial improvement of the worst predictions does merit consideration. For any calculation of vibrational lines it would appear imperative under the framework of this method.

However, there are other methods which one might employ to minimize the necessity for CI. As shown in extensive detail by Koutecký [7–9] a substantial effect on the importance of CI is exhibited by the choice of repulsion integrals. In the case of any particular molecule it would appear feasible to derive a best integral, based on his study, but a general applicability is quite doubtful: one would have to study every molecule in detail.

Much more promising could be the extension of the atomic orbital basis set to embrace $3p$ orbitals as questioned by Parr [4] and developed by Hartmann [16] within the framework of the Hückel method. These levels are only a few electron volts above the $2p$ states, and would probably not be much more difficult to treat than the triply-excited configurations.

However, most hopeful of all is recent work such as that of Rossi [17] in a new approach to a problem first studied by Roothaan [18]. He points the way to an SCF treatment of the open-shelled states. Whereas relatively few excited configurations would be possible in any CI treatment including $3p$ or higher orbitals as in the former treatment, the latter would not be restrictive. It would thus allow one to ascertain the constancy or reliability of comparatively limited treatments.

Acknowledgements. We are indebted to the National Science Foundation for partial support of this research (NSF grant GP 4290). T.W.S. was the holder of an NSF predoctoral fellowship 1965–1967. We also wish to acknowledge the help of Dr. Walter Hoffman and the staff of the Wayne State University Computing Center, and the computing time which they made available to us for this work.

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