Theoret. chim. Acta (Berl.) 3, 375—377 (1965)

Relationes

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

Expanded Gaussian Orbitals and the Electronic States of Ethylene

By

R. R. Hart and **M. B. Robin**

The recent resurgence of interest in the use of Gaussian-type basis orbitals (GTO's) for SCF treatments of electronic and molecular structure should become even more marked with the availability of the convenient GTO program package POLYATOM [*1*]. Recently, Moskowitz and Harrison [*3*] (MH) used POLYATOM for a wide variety of calculations on ethylene, as somewhat of a test case for the use of GTO's in polyatomic molecules. Although not in outstanding agreement with experiment, their spectral predictions are surprizingly similar, though calculated from basis sets of varied size. Thus, for bases ranging from 16 to 36 GTO's, the predicted $\pi \to \pi^*$ triplet and singlet excitations remain in the intervals 3.78 ± 0.32 eV and 10.28 ± 0.70 eV, respectively*, to be compared with the observed [*3*] excitation energies of 4.8 and 7.6 eV. Moreover, a massive configuration interaction calculation involving several hundred excited configurations in the largest MH basis, 9-(5332)**, affected the predicted excitation energies only slightly [*4*].

It thus appears that in ethylene a small GTO basis yields spectral predictions not significantly different from those of a much more extended calculation, a seemingly encouraging situation. However, by the same token, the agreement between prediction and observation is only mediocre and would appear to persist in any GTO calculation.

Our point in this note is practical, and is directed at those using GTO's for the calculation of electronic spectra. We have found, contrary to the above, that small differences in the bases can, in fact, result in widely different spectral predictions. Having found that the spectral predictions do vary with choice of basis, we further suggest a prescription for choosing the GTO basis so as to improve the spectral predictions.

The basic idea is that it may sometimes be advantageous to use GTO basis functions more expanded in space than those dictated by the customary consideration of energy minimization. Such "expanded orbitals" neglect the ener-

---

* The predicted excitation energies quoted throughout this paper were obtained using Eq. (68) of C. C. J. Roothaan, Revs. mod. Physics **23**, 69 (1951).

** (5332) basis ≡ *five* s-type, *three* each p_x- and p_y-type, and *three* p_z-type GTO's on each carbon; *two* s-type GTO's on each hydrogen.

getically important inner shells, but may give a better description of the outer valence shells, which govern the chemical and spectroscopic properties of the molecule*.

This is strongly suggested by inspection of the results of any molecular GTO calculation in which the exponents were selected, as usual, to minimize the SCF energy ("energy-minimized exponents"). In these calculations, the inner MO's, and particularly those corresponding to the 1*s* atomic orbitals, are well represented indeed, since their low orbital energies make the most important contribution to the SCF energy. By contrast, the chemically and spectroscopically more interesting outer MO's (and *a fortiori* the spatially yet more extended unoccupied MO's) though composed of the most expanded GTO's of the basis, are seen to be quite compressed therein, and apparently require several more GTO's with smaller exponents (and hence a wider extension in space) for their adequate description.

The detailed results presented by KRAUSS [2], for example, for the occupied MO's of first row hydrides using energy-minimized exponents in a GTO basis, clearly show the effect we mention above. In particular, the above comments also hold for the orbitals derived from the energy minimized MH 2-(3221) and 9-(5332) ethylene bases. A comparison of the MH bases shows that they vary mostly in how finely the *same* region of exponent space is covered, but little in the size or location of the region. Thus, the requirement that the least interesting innermost electrons be best represented in the energy-minimized bases, regardless of basis size, leads to the neglect of the orbital tails, a defect easily remedied by using expanded GTO's.

In order to explore the utility of such expanded orbitals, we have carried out over 15 POLYATOM calculations on $H_2C = CH_2$, $HN = NH$ and $H_2C = O$, noting the differences in the spectra predicted with and without expanded orbitals. Following the recalculation of the ethylene spectrum in the above two MH bases, an ethylene calculation was carried out in the following expanded (3221) basis: C *s*-type – 9.00, 0.32, 0.035; C *p*-type – 0.80, 0.08; H *s*-type – 0.17. These exponents were selected by inspection of KRAUSS' results, of results from unpublished $CH_3^\pm$ calculations, and of the MH molecular orbitals. In this way, the values of exponents required to adequately represent the higher energy MO's were determined. This calculation in the expanded (3221) basis yielded 4.67 eV and 7.96 eV for the $\pi \rightarrow \pi^*$ triplet and singlet excitation energies, in obviously improved agreement with the experimental values given above. In addition the ordering of the σ excitations changed dramatically. The lowest $CH \rightarrow CH^*$ and $\pi \rightarrow CH^*$ excitations dropped from 16 eV and 12 eV in the MH bases, to 10 eV and 7 eV in the expanded bases, the $CH \rightarrow \pi^*$ excitation remaining rather unmoved at about 8 eV. Thus, according to the expanded orbital calculation, the $CH \rightarrow CH^*$, $\pi \rightarrow CH^*$ and $CH \rightarrow \pi^*$ excitations are all candidates for assignment in the vacuum

---

* Related comments have been made for GTO's by M. C. HARRISON, J. chem. Physics **41**, 499 (1964); and by e.g. W. A. SANDERS and J. O. HIRSCHFELDER, J. chem. Physics **42**, 2904 (1965), for Slater type orbitals. The difficulty of properly representing the outer, valence, electrons in an energy-minimized basis, is probably more acute for GTO's, since these exhibit the wrong behavior at large distances.

ultraviolet spectrum of ethylene*. Similar work on $HN = NH$ and $H_2C = O$ confirms the importance of expanded GTO's in spectral predictions.

In order to recover the better SCF total energy of the conventional (3221) basis, we also calculated ethylene in an augmented (3221) basis, consisting of the MH 2-(3221) basis augmented to a (5332) basis by the *addition* of spatially more expanded GTO's. The additional exponents were selected so as to continue the geometric progression formed (as is commonly the case with energy-minimized bases [*2*, *5*]) by the exponents of the conventional 2-(3221) basis. The results of this augmented basis calculation were semi-quantitatively those already obtained in the (3221) expanded basis, thus leading us to believe that a properly augmented, energy-minimized GTO basis can yield both an adequate total energy and good excitation energies.

Prof. JULES MOSKOWITZ and Dr. L. C. SNYDER have both contributed much to this note by way of discussion and technical help, and we wish to thank them.

---

* In fact, these calculations, together with unpublished calculations of transition moments, and other considerations, lead us to believe that the weak "mystery band" of mono-olefins in the 2300 – 2000 Å region, recently reassigned as a CH $\rightarrow \pi^*$ transition [BERRY, R. S.: J. chem. Physics **38**, 1934 (1963)], is due to the $\pi \rightarrow$ CH* transition [ROBIN, M. B., R. R. HART, and N. A. KUEBLER (to be published)].

References

[*1*] CSIZMADIA, I. G., M. C. HARRISON, J. W. MOSKOWITZ, S. SEUNG, B. T. SUTCLIFFE, and M. P. BARNETT: "Program Set for Non-Empirical Molecular Calculations POLYATOM", program QCPE 47 A of the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, U.S.A.

[*2*] KRAUSS, M.: J. Res. nat. Bur. Standards **A 68**, 635 (1964).

[*3*] MOSKOWITZ, J. W., and M. C. HARRISON: J. chem. Physics **42**, 1726 (1965).

[*4*] — private communication.

[*5*] REEVES, C. M., and M. C. HARRISON: J. chem. Physics **39**, 11 (1963).

(Received August 26, 1965)