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Mechanized Molecular Calculations—The POLYATOM System

Michael P. Barnett
Solid State and Molecular Theory Group, Department of Physics, Massachusetts Institute of Technology

A SYSTEM of programs is being written by Dr. Malcolm C. Harrison, Dr. Jules W. Moskowitz, Dr. Brian T. Sutcliffe, D. E. Ellis, and R. S. Pitzer, to perform nonempirical calculations for small molecules. The system will consist of several major blocks which are listed below. It will be possible to use these in a fully automatic manner, or under manual control, by the provision of appropriate master programs and linking parameters. The system is being coded in FORTRAN for the IBM 709/90 computers. It is designed to allow independent modification and refinements of the individual blocks of the system, and to allow easy expansion to include further blocks as these are developed.

A procedure that can be used to perform molecular calculations has been described by S. F. Boys and G. B. Cook [Rev. Mod. Phys. **32**, 285 (1960)], and the initial structure of the POLYATOM system will correspond to this procedure in many respects. A similar system has been developed previously at the University of Leeds, see C. M. Reeves and M. C. Harrison, J. Chem. Phys. (to be published).

The main blocks of the initial system will be as follows: (1) an input program, to store the nuclear coordinates and orbital parameters of the basis functions, with their transformation properties; (2) an integral list generator, to construct a list of the names of the integrals that are needed between basis functions. This list will omit the names of zero integrals, and will associate the names of integrals that are equal due to symmetry; (3) an integral evaluation program, that will evaluate the necessary integrals. A program to compute integrals between atomic Gaussian orbitals is in operation. Existing programs to compute integrals between K- and L-shell Slater orbitals will be generalized to deal with orbitals of arbitrary quantum number; (4) an SCF program. Existing programs developed by C. A. Christy will be generalized to deal with closed- and open-shell systems in a more fully automatic manner. It is expected that several SCF programs will be written to deal with basis sets of different sizes. One such program will deal with basis sets that are small enough to allow all the relevant integrals to be kept in high-speed storage simultaneously. Another program will assume the basis set to be of arbitrary size; (5) a program to transform one- and two-electron integrals from one basis to another. This is in operation; (6) a codetor list generator to read or generate a list of functions that are to be used in a configuration-interaction calculation, and which are expressed in the codetor notation of Boys; (7) a formula generator to construct the formulas for the matrix elements between codetors in terms of the integrals over molecular orbitals; (8) a matrix generator to compute the matrix elements between codetors from the values of the molecular integrals; (9) a program to solve the secular equation; (10) a program to form density matrices, dipole moments, and related physical properties.

The programs that are being coded first will limit the basis set to 50 elements, so that certain sets of intermediate results can be kept in core storage concurrently. Considerations of computing time and of round off errors make it reasonable to limit the initial programs in this way. The fragmentation of the program in blocks that are compiled separately, and the use of a standardized format for the storage of intermediate results on magnetic tape, will make it possible to replace existing blocks of programming by others that do not limit the basis set, if this becomes expedient.

It is hoped that various refinements will be introduced at a later juncture and that these will include the use of exclusive orbitals, as defined by Boys, mixed Gaussian-exponential basis sets, and orbitals with explicit correlation factors.

Multicenter integrals between Slater orbitals are computed at present by a set of programs that are available for distribution as four self-contained binary decks to be run under the standard IBM Monitor Fortran system on any 709/90. These four decks may be used, respectively, to compute: (1) three-center resonance integrals involving K- and L-shell orbitals; (2) three-center Coulomb ($aabc$) integrals involving K- and L-shell orbitals; (3) three-center exchange ($abac$) integrals involving K- and L-shell orbitals; (4) four-center integrals involving s orbitals of principal quantum number not exceeding 12.

Arbitrary geometrical configurations of the nuclei are allowed in all cases. The format of the data cards that these programs read is described in MIT CCL

Technical Note No. 23. Source program listings are available. Further programs still being tested compute four-center integrals between $2p\pi$ orbitals centered on coplanar nuclei. Three significant figure agreement has just been obtained with results of Shavitt for a benzene integral, and better accuracy is expected when more terms are taken in the infinite series.[1] A check that can be made on integrals evaluation is illustrated by the data that is given below. If k_1 is the screening parameter in one of the orbitals in a molecular integral, the corresponding integral with k_1 replaced by $k_1 + h$ but all other parameters unchanged can be expanded as a Taylor series in h. The coefficients of successive powers of h are integrals in which the principal quantum number of the orbital containing k_1 as screening parameter takes successive values. The four-center integrals containing 4 $1s$ orbitals and one of the screening parameters (k_1) equal to 1.01 and 1.1 were computed directly and by the Taylor series expansion about $k_1 = 1$. Agreement was obtained of 2×10^{-7} in integrals of the order of magnitude 0.175. Three terms were needed for $k_1 = 1.01$, and 7 terms for $k_1 = 1.1$. This test involved computing integrals that contain $1s, 2s, \cdots, 7s$ orbitals.

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[1] *Note added in proof.* Five- to six-figure agreement has now been obtained.

Discussion on Molecular Spectra

THEODORE FÖRSTER, *Chairman*

MURRELL: [Summary of Lecture, "Quantitative Evaluation of Substituent Effects by Electronic Spectroscopy"]: It can be seen from experimental data that the substituent shifts in the frequency of the absorption bands of aromatic hydrocarbons can be divided into two parts. The evidence for this is that in the poly homo-substituted benzenes the total shift in the 2600 Å band is a sum of one part which is proportional to the number of substituents in the ring and another which depends on the relative position of the substituents. The relative contributions of these two parts depends on the substituents: Methyl and chloro substituent shifts consist mainly of the first (additive) part; fluoro and aza substituent shifts consist mainly of the second. Further evidence is obtained by comparing the effect of substituents on the spectrum of alternant and nonalternant hydrocarbons (say, naphthalene and azulene). A phenyl group has a larger effect on naphthalene than on azulene. A methyl group either gives a bathochromic or hypsochromic shift to the azulene visible band, depending on the position of substitution, whereas it always gives a bathochromic shift to the bands of alternant hydrocarbons.

From an analysis of the experimental data one can obtain parameters which can be associated with the inductive and mesomeric effects of the substituents, defining these terms in a way which is consistent with the qualitative definitions used by chemists.

A full account of the lecture is published in the Journal of the Royal Institute of Chemistry. [J. N. Murrell and K. Lenore McEwen, J. Chem. Phys. **25**, 1143 (1956); John Petruska, J. Chem. Phys. **34**, 1120 (1961); D. T. Clark, J. N. Murrell, and J. M. Tedder, J. Chem. Soc. 1250 (1963); J. N. Murrell, J. Roy. Inst. Chem. (to be published).]

BLOOR: At the Research Council of British Columbia we have been calculating substituent effects on the general case of the disubstituted benzenes of which the examples of the nitroamino compounds are a specific example. Two main approaches have been tried: 1. We have calculated molecular orbitals and excited states of two fragments R and X of a molecule $R - X$ by the Pople–Pariser–Parr–SCF method and then carried out configuration interaction calculations between the locally excited configurations of R and X and electron transfer configurations R^+X^- and R^-X^+. Our approach differs principally from Murrell's in the treatment of the inductive effect which is included only as a second-order perturbation and by including interaction of the electron transfer configuration with the ground state, which is ignored by Murrell. However, our conclusions using the method are substantially the same as those of Murrell; 2. In the second method we have carried out SCF calculations on the disubstituted benzene using parameters chosen to give correct excitation energies of the appropriate monosubstituted benzenes. Such calculations so far carried out give excellent agreement for the paradisubstituted benzenes but it appears that the method overemphasizes the interaction of the two substituents when they are orientated into ortho and meta positions relative to each other. These results are being prepared