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The Use of the CNDO Method in Spectroscopy.
X. The Calculation of the Self-Consistent Doublet and Triplet States

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A method is reported for calculation of a series of self-consistent excited doublet and triplet states by the CNDO/S method. Various problems of obtaining convergence are discussed, and examples are given of the rates of convergence in various manners of performing these calculations. The handling of symmetry is discussed, and it is shown how symmetry properties are used to make many states amenable to calculation by the variational principle.

We would like to report an extension of the CNDO/S method [1] for the calculation of spectra to open-shell systems, and in particular to the direct minimization and self-consistent calculation of doublet and triplet states. We have now developed a method by which we are in a position to make a direct minimization of doublet and triplet states of molecules by the restricted Hartree–Fock method [2]. Although the method of calculation is probably general, we have worked entirely within the CNDO/S scheme of semi-empirical parameterization.

The open-shell method used is that of Roothaan [2], which, of course, is not new. However, we believe that we have for the first time achieved the calculation, for large molecules, of not only the lowest state of a given manifold but of a whole series of states, provided they can be described in terms of a single configuration, that is, a single Slater determinant. A number of serious computational problems arise in these calculations, and in this paper we would like to report on the handling of these.

Preliminary results for a few compounds have already been reported [3–5], and further extended numerical results will be reported elsewhere [6].

ORBITAL CROSSING

In early attempts to do open-shell calculations for the lowest triplet states of some azines, we ran into serious convergence problems. These problems were readily identified as arising from a crossing of orbital energy levels during the iterative process of calculation; thus, when the highest two occupied orbitals are energetically close to each other, as they are for instance in pyridine, upon iterative calculation of the lowest triplet states we find that the lowest two orbitals sometimes cross in energy. If we use the molecular Aufbau principle to calculate the Fock matrix for the next iteration after such a crossing has occurred, we, of course, are beginning in effect a new calculation which attempts to converge on a different state than the one which the previous calculation approached. If the process of iteration is continued and the two orbitals continue to cross back and forth, we find that we alternately attempt an approach to the two states and, therefore, obtain a oscillatory behavior rather than a convergent one. Roothaan originally had proposed to overcome this problem by transforming the basis set of the calculation into a set of symmetry adapted orbitals. While such a calculation is perfectly feasible, it is unpleasant, requires a considerable amount of groundwork, and is difficult to program in a general fashion which is applicable to the different symmetry types of a given point group and to molecules in different point groups.

We have overcome this problem in an entirely different manner: we have programmed the symmetry behavior of our orbital into our program. The program first determines the point group under which the molecule in question, in the geometry assumed, transforms. We had previously incorporated this determination into our CNDO/S closed-shell program. Additionally, in this program we determine for each orbital the irreducible representation which has the same transformation properties as the orbitals. In the open-shell program we now make this symmetry determination at each iteration, and we enter into the program as input the number of doubly and singly occupied orbitals which transform as any given irreducible representation. With the symmetry behavior of each orbital available, we can now use the Aufbau principle separately for each irreducible representation having first enough orbitals doubly and then singly occupied to take care of all the electrons required in the configuration. Use of this technique has immediately eliminated all problems of orbital crossing.

HIGHER EXCITED STATES

With this symmetry determination of each orbital and the use of the Aufbau principle to the separate irreducible representations available, we are now in a position to specify not only the lowest excited state of any given multiplicity manifold but equally well higher configurations of such manifolds. Some restrictions still exist; thus for doublet states we can only calculate states described by two types of conficurations: (1) A states [7], in which an electron is promoted from a doubly occupied orbital to the orbital occupied by the single unpaired electron.

(2) *B* states, in which the single unpaired electron is promoted to a higher virtual orbital. The further restriction applies to both cases that the two orbitals involved in the transition transform as different irreducible representations, in other words that the transition is not totally symmetric. States in which an electron from a doubly occupied orbital is promoted to a virtual orbital are inaccessible to this calculation since for such states a single configuration gives rise, beside a quartet state, to two doublet states, neither of which can be expressed as a single determinant. Triplet states available to calculation include all those in which an electron from the highest doubly occupied orbital of any given symmetry type is promoted to the lowest virtual orbital of any symmetry type. Thus, for instance, in point group C_{2v}, which has four irreducible representations, we have accessible to calculation 16 singly excited triplet states provided both doubly occupied and virtual orbitals exist in each representation. For a C_{2v} molecule with a doublet ground state, we can calculate six singly excited doublet states. In principle, of course, we can also calculate many multiply excited states; such states, however, appear currently of little interest. Their calculation, which has been accidentally undertaken at times, has not produced any new problems or difficulties.

Convergence Problems

With the technique outlined, we have been able to make calculations for a large number of lower excited states of many molecules. However, we have found that for higher excited states we occasionally run into very serious problems of convergence and loss of symmetry. Both of these can be overcome by relatively simple means.

Loss of Symmetry

As iterations proceed, we have frequently noted that the accumulation of rounding errors has caused the symmetry of the orbitals to be lost so that a determination of the appropriate irreducible representations became impossible. The problem does not occur in every case but when it occurs, of course, it makes it impossible to proceed with the calculation. In order to overcome this problem, we have inserted a resymmetrization and renormalization procedure at each iteration at the point at which the symmetry of a given orbital is determined. All coefficients that should be numerically equal in an absolute sense are artificially made equal by averaging and the orbital is then renormalized. We have also demonstrated that in the converging cases this procedure has not led to any change of the results either in terms of energy or in terms of the density matrix obtained in the final result (cf. Table II below).

CONVERGENCE PROBLEMS

While we have never in the many thousands of calculations we have made in closed-shell systems encountered a case which failed to converge, in the open-shell system we have found that some calculations fail to converge. The failure to converge is normally signalled by a sharp increase in total energy which is accompanied by an oscillatory behavior of total energy. Examination of the density matrix shows that in such cases, the entire charge of the molecule at alternate iterations resides in one or another half of the molecule. We have attempted a number of routes to overcome this problem. While we have no guarantee that any of our solutions will work in every case, we have found that we have been able to achieve convergence in each case attempted by one or another of these techniques.

INITIAL DENSITY MATRIX

The Fock Matrix for the first iteration and the closed-shell CNDO/S program is generated from a diagonal density matrix in which each orbital has a number of electrons corresponding to the atomic number of the atom on which it resides. Orbitals are entirely filled with whole numbers of electrons and no special effort is made to evenly distribute electrons where some orbitals would otherwise be doubly, others singly occupied. We shall refer to this type of initial density matrix as a diagonal density matrix. In the closed-shell method, this has never caused any problems. Use of this diagonal density matrix is equivalent to the performance of a Hückel calculation as a first step, and use the resulting density matrix to initiate the iterative SCF calculation. We believe that our procedure, besides simplicity, has the advantage over an external Hückel calculation that the parameters are automatically chosen to be consistent with the later steps.

Our first attempt to overcome our convergence problems was to start, not with a diagonal density matrix, but to begin iterations with the density matrix of the ground state molecule. For this purpose, a ground-state calculation was first performed, the density matrix written on tape or disk and then used in the open-shell calculation. We found that in a number of cases, this procedure permitted very rapid convergence; however, in others the same divergent behavior recurred. Thus, this appears to be an expedient which is sometimes useful but which will not provide a general solution.

An alternate to this procedure has been to begin iteration with the density matrix of the corresponding state derived from a virtual orbital calculation. For this purpose, the ground-state wave functions were written on disk and used to generate a density matrix for the first orbital iteration. This expedient, although apparently sounder in principle, had no apparent advantage over the density matrix procedure. Examples of both procedures at work are given in Table III (below).

DENSITY MATRIX AVERAGING

In closed shell CNDO/S calculations, considerable convergence problems have been encountered, particularly when using the Mataga–Nishimoto approximation[1] to electron repulsion integrals [8]. The most common inhibition of rapid convergence appears to be an oscillatory behavior resembling that of an undamped spring. Although several elegant methods to improve convergence of iterative SCF procedures exist in the literature [9], we have devised a particularly simple and convenient one, which has the added advantage not to require extra storage in the computer.

This method consists of averaging the density matrix of the nth and $(n-1)$th iteration before calculation of the Fock matrix for the $(n+1)$th iteration. To apply this averaging procedure only when an oscillating convergence is encountered, two tests are introduced:

$$| E_n - E_{n-1} | > | E_n - E_{n-2} |, \tag{1}$$

$$(E_n - E_{n-1})(E_n - E_{n-2}) < 0, \tag{2}$$

where E_i is the total electronic energy obtained in the ith iteration. If the condition of Eq. 1 is satisfied, an oscillatory behavior obtains; if the condition of Eq. 2 is satisfied, the calculation appears to be on a converging path. In the closed-shell program, if both conditions are satisfied, all elements $P_{\mu\nu}^{i}$ of the density matrix of the ith iteration are averaged with the corresponding elements $P_{\mu\nu}^{i-1}$ of the last previous iteration,

$$P'_{\mu\nu} = (P_{\mu\nu}^{i} + P_{\mu\nu}^{i-1})/2, \tag{3}$$

and the new density matrix $P'_{\mu\nu}$ is used in the generation of the Fock matrix for the $(i+1)$th iteration. In the closed-shell CNDO/S program, this density matrix averaging has improved rates of convergence by as much as a factor of 3. Both tests were needed, since density matrix averaging begun too early was much less efficient, and could even give rise to a considerable slow-down of convergence.

In the open-shell calculations, we have also introduced this same density matrix averaging. Here, again, we find that averaging forces convergence in some cases in which it does not otherwise occur. In some cases, an *apparently* converging [Eq. 2] oscillatory behavior [Eq. 1] is not attained until the calculation has apparently diverged. At this point, as indicated above, upon alternate iterations

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[1] Some laboratories have reported problems of failure to converge in the case of closed-shell ions. Although we cannot give a rationale for this procedure, our program sets up the original diagonal density matrix for the neutral compound corresponding to the ion and adjusts the total electron count at the first iteration. With this procedure, we have never failed to obtain convergence in a closed-shell ion.

the total electron population migrates from one half of the molecule to the other, and averaging the density matrices of two such divergent populations produces more reasonable density matrix; in some cases this procedure has led to convergence. However, it seems philosophically and economically unreasonable to go through a divergent path to attain convergence.

We finally removed the second test [Eq. 2] so that any form of oscillatory behavior would force density matrix averaging. We found that this was by far the best procedure. Under this procedure, density matrix averaging in the divergent case begins almost immediately, that is, after the third or fourth iteration, never allows the fully oscillating condition to arise, and has forced convergence in every case we have tried. It appears then that density matrix averaging together with the resymmetrizing of eigenvectors is the method of choice to accelerate and force convergence in these open-shell situations with which we are dealing here.

CONVERGENCE TESTS

We have tried three different types of convergence tests: (a) convergence by total energy; (b) convergence for all occupied orbital energies; (c) convergence of the density matrix. The total energy and orbital energy convergence tests are made to a relative precision. That is, the convergence condition is

$$| E_n - E_{n-1}/E_n | < \delta_1 , \tag{4}$$

$$\left.\begin{array}{ll} |(\epsilon_j{}^n - \epsilon_j^{n-1})/\epsilon_j{}^n | < \delta_2 & \text{for} \quad \epsilon_j{}^n > 1 \\ | \epsilon_j{}^n - \epsilon_j^{n-1} | < \delta_2 & \text{for} \quad \epsilon_j{}^n < 1 \end{array}\right\} \text{for all } j, \tag{5}$$

$$| P_{\mu\nu}^n - P_{\mu\nu}^{n-1} | < \delta_3 \qquad \text{for all } \mu \text{ and } \nu, \tag{6}$$

where $\epsilon_j{}^i$ is the orbital energy of the jth orbital after the ith iteration and δ_1, δ_2, and δ_3 are three constants. We usually use

$$\delta_1 = 0.0001, \qquad \delta_2 = 0.0001, \qquad \delta_3 = 0.001.$$

If the orbital energy is less than 1 eV absolute, the convergence test for the absolute value is uninteresting; with a range of orbital energies between −50 and +30 eV and an arbitrary origin, a relative test of values that are accidentally near 0 is of no interest. For density matrix convergence, an absolute test is used. We have found that orbital energy convergence, with the criterion given, in the open-shell cases requires many more iterations than total energy convergence. We have, however, verified that the variation of the total energy after its convergence has been reached until orbital energy convergence is reached is only of the order of a few hundredths of an electron volt (cf. Tables III and V). This does not exceed the precision of the calculations since the total energies calculated are of the order of thousands of electron volts and the precision of the calculations is estimated to be of the order of six significant figures. Thus, unless either orbital energies or the wave functions are of extreme importance, we believe that total energy convergence is sufficient. We further, in both the closed- and open-shell programs, are backing up the total energy convergence by a density matrix convergence. This sometimes requires a few, sometimes a significant number, of extra iterations but guarantees at least that the density matrices also have become self-consistent. We believe that with this we have been sufficiently cautious. We may add that in those cases where we average density matrices, we make one additional calculation at the end without averaging in order to be certain to have a self-consistent function.

RESULTS

In order to test the computational methods discussed in the previous section, we have undertaken an extensive series of calculations on the 16 available triplet states of the pyridine molecule and of the 7 accessible doublet states of the pyridine molecular ion. We have carried out these calculations under a series of ten different conditions. Table I lists all the various conditions used. It indicates whether or

TABLE I

The Conditions for Running the Various States of Pyridine and Azulene*

	Resymmetrization	Convergence	Density Matrix Averaging	Initial Density Matrix
A	–	O	—	D
B	–	O	—	GS
C	–	O	U	VO
D	+	O	—	D
E	+	O	R	D
F	+	O	U	D
G	+	O	—	GS
H	+	O	U	VO
I	+	T	—	D
J	+	T	—	GS
K	+	T	—	VO
L	+	T	R	D
M	+	T	R	GS
N	+	T	R	VO
O	+	T	U	D
P	+	T	U	GS
Q	+	T	U	VO

* See text for explanation of symbols.

not resymmetrization was done. In the column under density matrix, D indicates a diagonal density matrix, GS a ground-state density matrix, and VO a virtual orbital density matrix. Next, we indicate whether density matrix averaging was done and if so, whether it was subject to both conditions of Eqs. 1 and 2, called restricted and indicated by R, or only subject to condition of Eq. 1, called unrestricted and indicated by U. Finally, we indicate whether convergence was orbital convergence (O) or total energy convergence (T). Table II gives the number of iterations required to reach convergence for each of the 16 triplet and 7 doublet states in each of the ten sets of calculations. The letter "S" indicates that the symmetry failed to be obeyed after the number of iterations indicated in parenthesis.

TABLE II

The Number of Iterations Required to Obtain Convergence According to the Criteria Indicated in the Text Under the Conditions Indicated in Table I

	A	B	C	D	E	F	G	H	J	N
				(a) Pyridine triplets						
a_2b_1	18	11	9	18	14	—	12	—	9	9
a_2a_2	10	8	7	10	10	—	10	—	7	7
a_1b_1	29	27	16	29	15	—	15	—	12	12
b_1b_1	>40C	26	8	56	17	25	17	—	12	11
a_1a_2	15S	14	16	15	15	—	15	—	11	11
b_1a_2	S(9)	S(7)	S(7)	19	14	10	13	9	10	10
b_2b_2	S(5)	S(8)	S(7)	35	22	26	22	19	14	14
b_2a_2	S(7)	S(8)	S(9)	16	15	13	12	9	10	11
a_2a_1	S(17)	15	S(23)	19	27	—	27	20	17	17
a_2b_2	S(7)	S(8)	S(11)	21	24	20	24	16	11	11
b_1a_1	S(12)	S(11)	30	54	36	28	36	—	19	19
a_1a_1	S(9)	S(10)	S(22)	36	>40	33	58	48	27	27
a_1b_2	S(7)	S(8)	S(11)	21	24	20	24	16	11	11
b_1b_2	S(7)	S(9)	8	>75C	16	47	16	—	11	11
b_2a_1	S(5)	S(7)	S(4)	25	37	21	37	17	18	18
b_2b_1	S(5)	S(6)	S(4)	>75D	31	>75C	32	24	23	23
				(b) Pyridine molecular ions						
a_2(GS)	8	7	2	8	7	—	7	—	7	7
a_1(A)	14	14	14	14	13	—	13	—	11	11
b_1(A)	22S	17	11	22	10	—	10	—	13	13
b_2(A)	S(7)	S(6)	S(5)	15	14	11	14	9	11	11
b_1(B)	13	10	10	13	9	—	9	—	9	9
a_1(B)	S(7)	S(7)	S(5)	15	14	12	13	9	13	13
b_2(B)	S(7)	7S	S(6)	9	9	8	9	8	8	8

In no case were more than 75 iterations attempted; where a number of iterations is given with a $>$ sign, the letter "C" indicates that it appeared as if the calculation would converge on a larger number of itereations, while the letter "D" indicates that it was oscillatory and did not appear to be converging.

A few conclusions are immediately obvious. In the absence of resymmetrization in a large fraction of cases, the symmetry disappears and the calculation cannot be completed; this is particularly true the higher the energy of the state in question. Resymmetrization in those cases where convergence was obtained without it does not affect the number of iterations required and, as we will see below, does not affect the results of the calculation; see columns A and D. For this reason, calculations F were not performed on those cases in which calculations B had already converged, since it could be anticipated that the number of iterations and the results would be the same. Similarly, calculations H were not performed in those cases where calculation C had already converged. Next, it is obvious that overall the most rapid convergence is achieved by total energy convergence, columns G and J. It appears that the *manner* of density matrix averaging plays no role in the results as the two columns, F and E, which differ only by this factor, are nearly the same. The effect of the initial density matrix can be obtained from the comparison of columns D and G and of columns F and H. In some cases, the improvement appears dramatic, in others marginal. If account is taken of the fact that the generation of an original density matrix requires a special calculation for the ground state, the writing of the density matrix or of the wave function on disk, and the rereading of this information from disk, it seems that the improvement is probably not sufficient to be worth using routinely unless a large number of states are calculated simultaneously.

Table III gives the total electronic energies for all calculations that have converged; actually, the energies are of the order of -3470 eV, but only the last five significant figures are listed, without sign. Even a cursory examination of this table indicates unambiguously that the total energy is completely independent of the method of calculation used and the number of iterations required. In no row of the table are the deviations greater than one in the sixth significant figure. Most of them vary only by a few thousandths of a volt. If it is remembered that these calculations were performed on a 32-bit IBM machine, with a precision of slightly over seven significant figures, in single precision, with only the Givens Householder matrix diagonalization in double precision, these results are extremely comforting. It can certainly be concluded that the results for pyridine are reproducible to a minimum of six significant figures. This, of course, does not imply an accuracy to the tenth of the electron volts since there are systematic approximations made which seriously put an accuracy of this sort in doubt.

It is particularly instructive to compare the results of columns A and D, that is, the results obtained with or without resymmetrization. Obviously, there is no

TABLE III

The Energies Obtained for Pyridine at Convergence Under the Various Conditions Indicated in Table I. Energies given are $-E - 3400.000$ eV.

	A	B/F	C/H	D	E	G	K	N
				(a) Pyridine triplets				
a_2b_1	70.963	70.962	70.962	70.964	70.962	70.961	70.959	70.962
a_2a_2	70.830	70.831	70.827	70.831	70.831	70.831	70.827	70.827
a_1b_1	70.609	70.611	70.610	70.610	70.608	70.608	70.608	70.608
b_1b_1	—	70.383	70.385	70.384	70.384	70.384	70.383	70.380
a_1a_2	69.631	69.929	69.628	69.630	69.628	69.628	69.628	69.628
b_1a_2		69.368	69.367	69.369	69.368	69.368	69.365	69.366
b_2b_1	—	—	67.663	—	67.664	67.663	67.667	67.667
b_2a_2		67.204	67.196	67.205	67.196	67.198	67.200	67.198
a_2a_1	—	66.464	66.461	66.465	66.461	66.461	66.462	66.462
a_2b_2	—	65.826	65.823	65.825	65.825	65.824	65.823	65.826
b_1a_1	—	65.556	65.559	65.557	65.559	65.559	65.555	65.555
a_1a_1	—	65.431	65.431	65.431	65.433	—	65.434	65.434
a_1b_2	—	64.885	64.886	64.886	64.888	64.888	64.885	64.885
b_1b_2	—	64.495	64.497	—	64.491	64.492	64.492	64.492
b_2a_1	—	63.351	63.355	63.356	63.355	65.355	63.353	63.353
b_2b_1	—	62.386	62.379	62.385	62.381	62.381	63.382	63.382
				(b) Pyridine molecular ions				
a_2(GS)	64.369	64.368	64.369	64.368	64.366	64.366	64.368	64.368
a_1(A)	63.604	63.604	63.602	63.604	63.601	63.601	63.604	63.604
b_1(A)	—	63.242	63.242	63.243	63.239	63.239	63.243	63.243
b_2(A)	—	61.222	61.221	61.224	61.220	61.221	61.220	61.221
b_1(B)	59.422	59.419	59.421	59.421	59.420	59.420	59.420	59.420
a_1(B)	—	55.514	55.514	55.514	55.512	55.513	55.511	55.511
b_2(B)	—	55.052	55.053	55.052	55.052	55.052	55.052	55.052

fundamental theoretical validity of the resymmetrization procedure; it is purely empirical. However, Table III shows clearly that the results in total energy are indistinguishable whether or not this procedure is invoked, provided the convergence occurs in either case. Additionally, we have compared the electron densities obtained from the density matrix in these cases. These are identical to at least three significant figures. We have further compared the energies iteration by iteration of the cases in which the symmetry disappeared after a number of iterations. As long as the symmetry was obeyed, no significant differences in total energies or in electron densities could be discerned. This then provides justification for using this empirical adjustment without which the calculations in most cases become impossible.

The pyridine calculations, however, have provided very little insight into calculations that do not readily converge. Only a single state, the b_2b_1 configuration, appears to fail to converge, and only under one set of conditions, a set involving no density matrix averaging and the use of the diagonal density matrix as a starting point. In connection with some other work, we have had occasion to run all triplet states of azulene. In these calculations, five states gave us problems in convergence. We have taken these five plus three other states and subjected them to a similar analysis through many different manners of calculation. Since, at this point, we had decided that resymmetrization was essential and that total energy convergence was sufficient, and since calculations on the much larger azulene are more expensive, we have restricted the set of conditions in these two respects. Since the pyridine results gave no indication as to the best manner of handling two of the possible variation considered: the *type* of initial density matrix used and the *manner* of density matrix averaging, we have consequently used the azulene calculations to carefully test these two variables. The results for the number of iterations required to obtain convergence are listed in Table IV. It is immediately obvious the density matrix averaging is required to get reasonable convergence as indicated by columns I, J, and K.

TABLE IV

The Number of Iterations Required to Obtain Convergence for Eight Triplet States of Azulene Under the Conditions Indicated in Table I. (D means Divergence that goes into Oscillation.)

	I	J	K	L	M	N	O	P	Q
a_2b_1	14	13	12	9	10	9	9	10	9
b_2b_1	27	24	23	14	14	13	12	14	13
b_2a_2	20	14	13	16	12	11	16	12	11
a_2a_1	16	D	D	18	D	D	18	19	18
b_1a_1	D	D	D	16	28	27	16	15	20
b_2a_1	D	D	15	33	16	15	D	14	15
a_1a_1	D	D	31	30	32	31	D	16	31
a_1b_2	D	34	11	15	12	11	15	12	33

Unfortunately, there is no unambiguous choice among the nine methods listed in Table IV. No single set of conditions seems to be clearly superior to any other. Overall, the best results seemed to be obtained in columns P and Q, that is, by reading in either the ground state or the virtual orbital density matrix, and proceding with an unrestricted density matrix averaging. However, we have seen before that unrestricted density matrix averaging can also lead to problems, and column O shows two cases of divergence. Overall, then, we believe one must conclude that there is no single set of conditions that can at this point be considered unambiguously superior or to guarantee convergence. For economy reasons, we believe the diagonal density matrix with restricted averaging is probably the best starting point. It gives convergence in most cases and for the states of low energy which are most often of interest and in a relatively low number of iterations, although for some situations the number of iterations is substantially higher than in some of the other options. Only if convergence problems are encountered here do we believe that it is indicated to write a density matrix or a wave function on disk and then proceed with unrestricted density matrix averaging from such a starting point. Which of the two is better, we cannot specify with the limited experience at hand.

TABLE V

The Energies Obtained from the Calculation on Eight Triplet States of Azulene Under the Conditions Indicated in Table I. Energies listed are $-E$-7000.000 eV.

	I	J	K	L	M	N	O	P	Q
a_2b_1	52.887	52.859	52.859	52.867	52.871	52.879	52.867	52.871	52.879
b_2b_1	50.359	50.355	50.363	50.375	50.344	50.355	50.387	50.340	50.363
b_2a_2	50.313	50.305	50.305	50.316	50.31	50.320	50.316	50.313	50.305
a_2a_1	45.695	—	—	47.684	—	—	47.684	47.688	47.691
b_1a_1	—	—	—	46.875	46.875	46.875	46.875	46.902	46.875
b_2a_1	—	—	—	45.480	45.480	45.488	—	45.461	45.488
a_1a_1	—	—	—	44.574	44.574	44.574	—	44.566	44.574
a_1b_2	—	44.363	44.363	44.301	44.344	44.344	44.301	44.344	44.344

Table V lists the energies to which the azulene calculations have converged. It is noticed that the constancy in this case is not quite as good as in pyridine. Since the total electronic energy is about twice that of pyridine, we might have anticipated errors to be of about twice the magnitude. Unfortunately, this is not true. The variations among these nine methods in energies reached a maximum of 0.05 volts although generally they are more within the range of 0.02 volts. It maybe that the choice of conditions is, in effect, wider in these experiments than they were in the pyridine case, or it may be that the uncertainty rises faster than linear with molecular size. However, certainly these data indicate that even in azulene we can put confidence into our energies to better than 0.05 eV.

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References

1. J. Del Bene and H. H. Jaffe', *J. Chem. Phys.* **48** (1968), 1807; **48** (1968), 4050; **49** (1968), 1221; R. L. Ellis, G. Kuehnlenz, and H. H. Jaffe', *Theoret. Chim. Acta* **26** (1972), 131.
2. C. C. J. Roothaan, *Rev. Mod. Phys.* **32** (1960), 179.
3. H. M. Chang and H. H. Jaffe', *Chem. Phys. Letters* in press.
4. H. M. Chang, H. H. Jaffe', and C. J. Seliskar, *J. Amer. Chem. Soc.* in press.
5. H. H. Jaffe', C. A. Masmanidis, H. M. Chang, and R. L. Ellis, *J. Chem. Phys.* in press.
6. H. M. Chang and H. H. Jaffe', to be published.
7. P. Balk, S. DeBruim, and G. J. Hoijtnik, *Rec. Trav. Chim.* **76** (1957), 907; A. Ishitani and S. Nagakura, *Theoret. Chim. Acta* **4** (1966), 236.
8. K. Nishimoto and N. Mataga, *Z. Physik. Chem. (Frankfort)* **12** (1957), 335; **13** (1957), 140.
9. See, for example, W. J. Hunt, W. A. Goddard III, and T. H. Dunning Jr., *Chem. Phys. Letters* **6** (1970), 147.