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Electronic Structures of Unsaturated Molecules Containing Hetero-atoms, — Configuration Interaction Treatment Including Doubly Excited Configurations

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The π-electron structures of several unsaturated molecules containing hetero-atoms were studied by SCFMO-CI scheme employing the Pariser-Parr-Pople method, special attention being paid to the effect of doubly excited configurations upon calculated transition energies, transition moments and π-electron distributions in the ground and lower excited states. The transition energies and oscillator strengths calculated for pyridine, phenol, aniline, pyrrole and furan were compared with their experimental values. Consequently, the inclusion of doubly excited configurations was found to improve the coincidence between the theoretical and observed values and to remove some difficulties in the application of the Pariser-Parr-Pople method to molecules containing hetero-atoms. One-center integrals W_P and γ_{PP} for hetero-atoms were taken as parameters in the calculations of phenol and aniline. Their fittest values were determined reasonably to be $W_N=-24.71$, $W_O=-30.08$, $\gamma_{NN}=13.75$, and $\gamma_{OO}=16.78$ eV.

The Pariser-Parr-Pople (P-P-P) method[1,2] has been successfully applied to many unsaturated organic molecules. The adequateness of several approximations adopted in this method has been discussed from several points of view. For example, the adequateness and limitations of the zero differential overlap approximation have been studied by use of the Löwdin orbitals.[3,4] Furthermore, the I-A approximation for the one-center Coulomb repulsion integrals has been discussed on the basis of the correlation effect,[5] the σ-π interaction,[6] and the expansion of excited orbitals.[7]

One of the fundamental problems of the P-P-P method is the treatment of the σ-π interaction, especially of the change in the σ-core caused by π-electron excitation. The development of the CNDO method[8] and other theoretical calculations including both σ and π electrons has brought about some progress in the direction of overcoming this difficulty.

Another important problem is concerned with the application of the P-P-P method to molecules containing hetero-atoms. The results calculated for them are generally sensitive to parameters. Several methods have been presented for the purpose of improving the prediction and interpretation of charge distributions in the ground states of the molecules. They include the VESCF method by Brown and Heffernan[9] and the method of in-

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[1] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953), 767 (1953).

[2] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1357 (1953).

[3] R. McWeeny, *Proc. Roy. Soc.* (London), **A227**, 288 (1955).

[4] I. Fischer-Hjalmars, *J. Chem. Phys.*, **42**, 1962 (1965); "Advances in Quantum Chemistry," Vol. II, ed. by P. O. Löwdin, Academic Press Inc., New York (1965), p. 25.

[5] T. Arai and P. Lykos, *J. Chem. Phys.*, **38**, 1447 (1963).

[6] M. O. Orloff and O. Sinanoglu, *ibid.*, **43**, 49 (1965).

[7] S. Huzinaga, *ibid.*, **36**, 453 (1962).

[8] J. A. Pople, D. P. Santry and G. A. Segal, *ibid*, **43**, S129 (1965).

[9] R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

cluding penetration integrals.[10] Furthermore, continuing efforts have made to find improved methods which give reliable results to excitation energies of molecules containing hetero-atoms, and consequently some progress has been achieved in the direction of determining appropriate core resonance integrals[11,12] and of considering the influence of electron cloud polarization upon the two center Coulomb integrals.[13] In the present study we undertake to make some contribution to this problem from the standpoint of attaching some importance to the configuration interaction (CI).

In the P-P-P type calculation, the CI procedure is usually made only among singly excited configurations (SECI treatment). The results in benzene[14-20] and other several hydrocarbons,[18-21] however, point out the importance of some doubly excited configurations. The CI procedure may be expected to have an important meaning in theoretical studies of the π-electron structures of molecules containing hetero-atoms. For example, if the core potential of a hetero-atom is too deep, the single configuration picture gives too large electron density on that atom, but the CI procedure relieves obviously this tendency. In addition, in molecules containing hetero-atoms, the charge distribution is not uniform, and is reorganized by a π-electron excitation. This reorganization in the molecules gives relatively larger effect on charge distributions in excited states and on π-electron levels than on those in hydrocarbons. This effect can be taken into account by the CI procedure. In the present paper, we study the effect of CI including the doubly excited configurations upon the calculated results of π-electron levels, transition moments and electron distributions in some molecules, paying a special attention to the parameters associated with hetero-atoms.

Method of Calculation

In the present study, pyridine, aniline, phenol, pyrrole and furan were taken as the typical molecules containing hetero-atoms and their π-electron structures were calculated by the P-P-P method combined with CI including doubly excited configurations (DECI treatment).

In the evaluation of SCF orbitals of pyridine, the Pariser-Parr parameters[1,2] were employed; that is to say, one-center Coulomb integral γ_{pp} was taken to be the difference between the ionization potential I_{p} and the electron affinity A_{p} for an appropriate valence state, and the two-center Coulomb integral γ_{pq} was calculated by the uniformly charged sphere model with the effective nuclear charge Z_{p} determined by Salter's rule. Concerning W_{p} representing the diagonal matrix element of the χ_{p} atomic orbital with respect to the one-electron Hamiltonian consisting of the kinetic energy and the core attraction due to atom p, its absolute value was taken to be equal to the ionization potential of an appropriate valence state.

Several discussions have been made concerning the problem which $|W_{\text{p}}|$ value should be adopted for the nitrogen atoms of aniline and pyrrole, the first or second ionization potential. We have the same problem for the oxygen atoms of phenol and furan, too. Some authors insisted upon the superiority of using the first ionization potentials as the $|W_{\text{p}}|$ values of these atoms.[22,23] Our opinion is that the most suitable $|W_{\text{p}}|$ value for each of these atoms exists between the first and second ionization potentials. Therefore, we carried out several calculations for each of the aniline and phenol molecules, regarding the W_{p} and γ_{pp} values of the heteroatoms of these molecules as parameters. The best values determined for aniline and phenol were used for the calculation of pyrrrole and furan, respectively. The W_{p} and γ_{pp} values for the carbon atom and the γ_{pq} values necessary for the calculation of these four molecules were evaluated by the same procedures as described in the case of pyridine.

The core resonance integral (β_{CC}) for the carbon-carbon bond of the benzene and pyridine rings was taken to be equal to -2.61 eV. This value is the optimum one for interpreting the observed benzene spectrum.[24] The core resonance integrals necessary for the calculation of pyrrole and furan were evaluated by two formulas presented by

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10) J. D. Dahl and A. E. Hansen, *Theor. Chim. Acta*, **1**, 199 (1963).

11) See, for example, K. Ohno, "Advances in Quantum Chemistry," Vol. III, ed. by P. O. Löwdin, Academic Press Inc., New York (1967) p. 240.

12) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

13) K. Nishimoto, *ibid.*, **5**, 74 (1966); **7**, 207 (1967).

14) F. A. Gray, I. G. Ross and J. Yates, *Aust. J. Chem.*, **12**, 347 (1959).

15) T. Anno and A. Sado, *J. Chem. Phys.*, **39**, 2293 (1963).

16) W. E. Donath, *ibid.*, **40**, 77 (1964).

17) H. Itoh and Y. I'Haya, *Theor. Chim. Acta*, **2**, 247 (1964).

18) N. L. Allinger, J. C. Tai and J. W. Stuart, *ibid.*, **8**, 101 (1967).

19) J. Koutecky, J. Cizek, J. Dubsky and K. Hlavaty, *ibid.*, **2**, 462 (1964).

20) J. Koutecky, K. Hlavaty and P. Hochmann, *ibid.*, **3**, 341 (1965).

21) N. L. Alliger and T. W. Stuart, *J. Chem. Phys.*, **47**, 4611 (1967).

22) S. Kwiatokowski, *Theor. Phys.* (Poland), **13**, 817 (1965).

23) S. Kwiatokowski, *Acta Phys. Poland*, **27**, 477 (1966); **30**, 529 (1966).

24) H. Kashiwagi, presented at the Symposium on Molecular Structure and Spectroscopy, Sapporo, on October, 1967.

Mulliken[25] and by Ohno.[26] For the other molecules, the core resonance integral (β_{cx}) for the bond including the hetero-atom was regarded as a parameter.

In the CI calculation, we took all the singly and doubly excited configurations for pyridine, pyrrole and furan, but for phenol and aniline disregarded several doubly excited configurations which include the excitation from the lowest occupied orbital.*[1] These configurations are higher than the ground configuration by more than 16 eV and seem to have only little influence on lower excited states.

There are five types of doubly excited configurations,[27] and the total numbers of configurations taken in the actual calculation are 55 for pyridine, 58 for aniline and phenol, and 37 for pyrrole and furan.

In actual calculations we need the data on the geometrical configurations of the molecules under consideration. Pyridine and the benzene rings of aniline and phenol were assumed to have the same geometrical configurations as benzene, that is, all the bond lengths were taken to be 1.397 Å.*[2] The C–N and C–O bond lengths in aniline and phenol were assumed to be 1.38 Å and 1.36 Å, respectively, from those of similar compounds given in Sutton's table.[28] The structure of pyrrole was also taken from the same table. The calculation of furan was caried out on the basis of its geometrical structure determined by Bak *et al.*[29]

The computation was carried out by a HITAC 5020E located at the Computer Center, the University of Tokyo.

Results and Discussion

Effect of Parameters. The DECI treatment reduces somewhat the effect of the W_p value upon the calculated energy levels of lower excited states compared with the SECI treatment, (at least) when the change of W_p is limited to ± 4 eV. This is clear form Fig. 1 which exhibits, taking aniline as an example, the W_p dependency of lower excited levels calculated by the P–P–P method without CI and with the SECI and DECI procedures. The same tendency was found for the other molecules under consideration. It is noteworthy that the effect of W_p upon the calculated results is reduced by the DECI treatment.

The effect of one-center Coulomb integrals, γ_{pp}'s upon the calculated energy levels is scarcely reduced by the DECI treatment. Some energy levels are more sensitive to γ_{pp} in the DECI treatment than in the SECI one. This may conceivably be attributed to the fact that γ_{pp} contributes directly to the matrix element of the DECI calculation.

Concerning aniline and phenol, calculations were carried out by the use of several sets of the parameters, W_p and γ_{pp}, with the step of about 2 and 1 eV, respectively, and we looked for the most suitable set which gives the best agreement with the observed transition energies. Consequently, we obtained the values given in Table 1. The selected W_p values, as expected, are the intermediates between the first and the second ionization potentials. Kwiatokowski[22,23] calculated the tran-

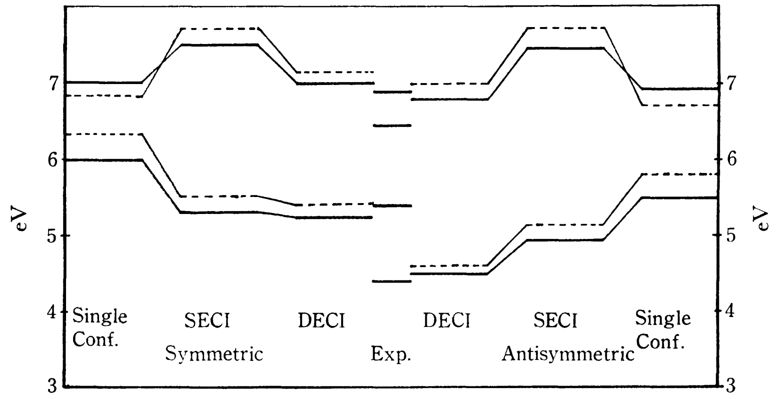

Fig. 1. Dependence of the calculated energy levels of aniline upon the W_N value.
——— $W_N=-26.71$, ········· $W_N=-24.71$

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25) R. S. Mulliken, *J. Chem. Phys.*, **46**, 521 (1949).

26) K. Ohno, *Theor. Chim. Acta*, **2**, 215 (1964).

*[1] This neglect reduces the time necessary for the CI calculation to about a half.

27) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).

*[2] According to Sutton's Table, the C–C bond lengths of pyridine are 1.3945 and 1.3944 Å and therefore the assumption on its geometry seems to be reasonable concerning the estimation of β_{CC}.

28) "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. by L. E. Sutton, the Chemical Society, London (1958) and its Supplement.

29) B. Bak, L. Hansen and J. Rastvup-Andersen, *Discuss. Faraday Soc.*, **19**, 30 (1955).

TABLE 1. SELECTED PARAMETERS FOR THE P-P-P CALCULATION INCLUDING DOUBLY EXCITED CONFIGURATIONS

Atom	From I_p and I_p-A_p		Optimized values	
	$\lvert W_p \rvert$	γ_{pp}	$\lvert W_p \rvert$	γ_{pp}
C	11.22	10.60b)	—	—
N pyridine type	14.12	12.34c)	—	—
pyrole type	28.71a)	16.75a,c)	24.71	13.75
O ketone type	17.70	15.23c)	—	—
furan type	34.08a)	18.78a,c)	30.08	16.78

a) W_p for these two cases is the second ionization potential, and γ_{pp} is the difference between the first and second ionization potentials.
b) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).
c) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

sition energies of aniline by the P-P-P method with the SECI treatment and using Nishimoto-Mataga's formula³⁰⁾ for γ_{pp}, and obtained the results coincident with the observed transition energies by adopting the $|W_N|$ value (22.49 eV) lower than the second ionization potential of nitrogen, and γ_{pp} for the neutral atom.*3 His parameter values are similar to ours, although the γ_{pp} value in the present calculation is a little greater than that of Kwiatokowski. Since in the SCF calculation the $(W_p + 1/2P_{pp}\gamma_{pp})$ is (P_{pp} is the π-electron density on atom p) mainly effective for the evaluated energies, there may be several sets of W_p and γ_{pp} to give a good agreement between the theoretical and experimental transition energies.

The absolute value of the core resonance integral β_{C-X} for aniline and phenol is somewhat larger in the DECI treatment than in the SECI one. The same tendency was found for β_{C-C}.15) For pyrrole and furan, the better results were obtained with the aid of the core resonance integrals derived by Ohno's formula than by Mulliken's formula, although the difference is rather small and too much

TABLE 2. EXPERIMENTAL AND THEORETICAL EXCITATION ENERGIES (ΔE, eV) AND OSCILLATOR STRENGTHS (f) OF PYRIDINE

Experimentala)		Mataga-Nishimotob)		Present work SECI		Present work DECI	
ΔE	f	ΔEc)	f	ΔEc)	f	ΔEc)	f
4.96	0.03	5.01(A)	0.024	5.01(A)	0.038	4.93(A)	0.030
6.36	0.20	6.25(B)	0.026	5.65(B)	0.02	6.26(B)	0.01
7.04	1.36	7.23(A)	1.04	7.30(A)	1.15	7.26(A)	1.09
		7.16(B)	1.24	7.49(B)	1.12	7.39(B)	1.01

a) B. Pickett and B. Pullman, "Quantum Biochemistry," Interscience Publishers, New York (1963).
b) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (Frankfurt), **13**, 140 (1959).
c) Symmetry of each level is shown in parentheses.

TABLE 3. EXPRIMENTAL AND THEORETICAL EXCITATION ENERGIES (ΔE, eV) AND OSCILLATOR STRENGTHS (f) OF ANILINE

Experimentala)		Fischer-Hjalmarsb)		Present work SECI		Present work DECI	
ΔE	f	ΔEc)	f	ΔEc)	f	ΔEc)	f
4.40	0.028	4.70(A)	0.015	4.68(A)	0.031	4.38(A)	0.020
5.39	0.144	5.58(B)	0.19	5.30(B)	0.220	5.27(B)	0.130
6.40	0.510	6.50(A)	0.55	6.82(A)	0.63	6.70(A)	0.430
6.88	0.570	6.67(B)	0.68	7.08(B)	0.73	6.91(B)	0.506
7.87	(0.68)	7.50(A)	0.61	8.29(A)	0.99	8.03(A)	0.510
		7.40(B)	0.41	8.37(B)		8.11(B)	

a) K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).
b) I.Fischer-Hjalmars, *Ark. Fysik*, **21**, 123 (1962).
c) Symmetry of each level is shown in parentheses.

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30) K. Nishimoto and N. Mataga, *Z. Physik. Chem.* (Frankfurt), **12**, 335 (1957).

*3 Exactly speaking, this corresponds to the γ_{pp} value for the anion.6)

TABLE 4. EXPERIMENTAL AND THEORETICAL EXCITATION ENERGIES (ΔE, eV) AND OSCILLATOR STRENGTHS (f) OF PHENOL

Experimental[a)]		Bloor, Peradedejordi[b)]		Present work			
				SECI		DECI	
ΔE	f	ΔE[c)]	f	ΔE[c)]	f	ΔE[c)]	f
4.59	0.020	4.80(A)	0.10	4.52(A)	0.037	4.66(A)	0.021
5.82	0.132	5.96(B)	0.60	5.16(B)	0.156	5.69(B)	0.159
6.70	0.636	6.82(A)	1.20	6.61(B)	0.950	6.92(A)	0.754
6.93	0.467	6.84(B)	1.09	6.74(A)	1.59	7.06(B)	0.840

a) K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).
b) J. E. Bloor and F. Peradejordi, *Theor. Chim. Acta*, **1**, 83 (1962).
c) Symmetry of each level is shown in parentheses.

TABLE 5 EXPERIMENTAL AND THEORETICAL EXCITATION ENERGIES (ΔE, eV) AND STATE SYMMETRIES OF PYRROLE

Experimental[a)]	Chiorboli *et al.*[b)]		Present work			
			SECI		DECI	
ΔE	ΔE	symm.	ΔE	symm.	ΔE	symm.
5.87	5.89	B_1	5.92	B_1	5.80	A_1
6.77	6.80	A_1	6.46	A_1	6.51	B_1
7.22	7.18	A_1	7.43	A_1	7.35	B_1
—	7.45	B_1	7.94	B_1	7.83	A_1

a) See Ref. 32
b) Ref. 32

TABLE 6. EXPERIMENTAL AND THEORETICAL EXCITATION ENERGIES (ΔE, eV) AND OSCILLATOR STRENGTHS (f) OF FURAN

Experimental[a)]		Suppenfield,[a)] Kreevoy		Present work			
				SECI		DECI	
ΔE	f	ΔE[b)]	f	ΔE[b)]	f	ΔE[b)]	f
6.05	0.12	5.92(A)	0.11	6.10(A)	0.20	5.89(B)	0.14
6.47	0.078	6.49(B)	0.07	6.53(B)	0.04	6.45(A)	0.10
7.55	—	7.—(A)	—	7.54(A)		7.36(A)	

a) D. S. Suppenfield and M. Dreevoy, *Tetrahedron*, **19**, Suppl. 2, 286 (1963). In this calculation, the following parameters were used and the penetration integrals were included: $\gamma_{OO}=14.79$ eV, $W_O=-34.16$ eV.
b) Symmetry of each level is shown in parentheses.

importance should not be attached to it.

Energy Levels. The energy levels calculated by the DECI method are shown in Tables 2—6, together with the experimental values and the results obtained by the SECI method. In these tables, the results obtained by other authors are also given for the purpose of compariosn, only one example being taken from many calculations for each molecule. The comparison of the energy levels calculated by the DECI method with those by the SCF scheme and by the SECI method are schematically shown in Figs. 2—5[*4] for pyridine, aniline, phenol and pyrrole. From these figures, it is clear that the energy levels changes to a considerable extent by the DECI treatment compared with the results by the SECI calculation. The DECI calculation stabilizes the ground states of these molecules by 0.5—1 eV and improves greatly the agreement between the theoretical and experimental excitation energies.

The most remarkable effect of the DECI treatment is found for the separation between the lowest and the second lowest excited states. In the case

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[*4] For the convenience of comparison, in these figures the energy levels calculated by the DECI treatment are corrected in such a way as the ground state is equal to that calculated by the SECI treatment.

of the SECI method, the calculated separation is too small compared with the observed value for pyridine, aniline and phenol. The DECI treatment improves this point to a great extent and gives the reasonable values. This is also the case for benzene.[15] In this connection, it is worth noticing that the great separtion between these two states can be obtained[29] by the SECI treatment, when we use Nishimoto-Mataga's formula[31] for γ_{pq} instead of the uniformly charged sphere model. The former gives the smaller γ_{pq} value by 1—2 eV than the latter in the important region of interatomic distance. This seems to mean that the inclusion of the doubly excited configurations has effectively the effect similar to that of the decrease in γ_{pq}. This may be a correlation effect by screening.[*5]

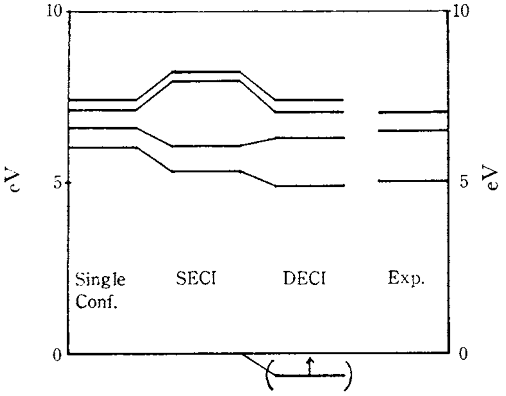

Fig. 2. Calculated Energy Levels of Pyridine.

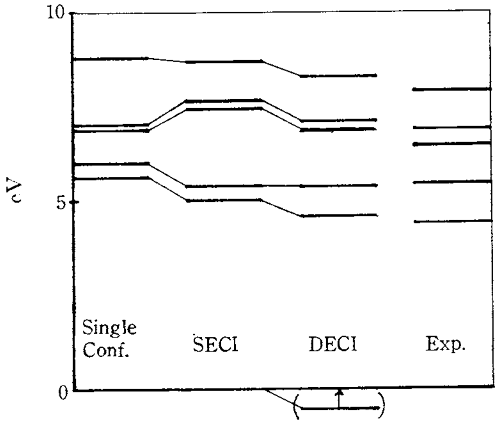

Fig. 3. Calculated and observed energy levels of aniline.

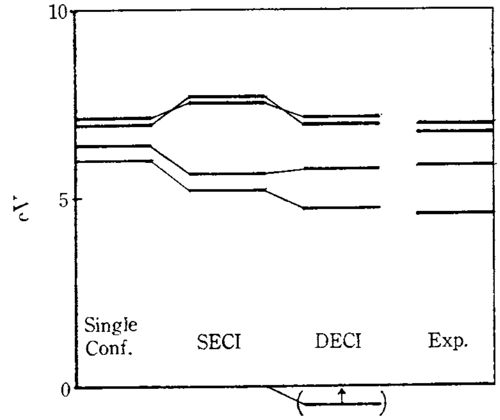

Fig. 4. Calculated and observed energy levels of phenol.

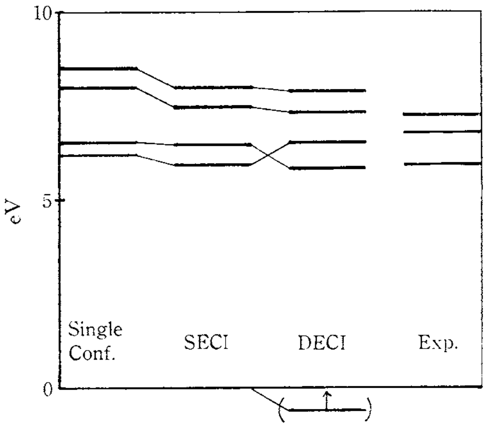

Fig. 5. Calculated and observed energy levels of pyrrole.

In phenol, the third and fourth excited levels are inverted in the DECI calculation compared with the result by the SECI treatment. Since the composite-molecule method[32] and also the modified P-P-P method[12] support the results of the DECI treatment, this inversion is thought to be rather important.

In our calculation, the higher excited levels evaluated for aniline and phenol have a tendency to be a little higher than the observed ones. In order to lower these levels, it may be necessary to take doubly excited configurations higher than those taken in the present calculation.

In pyrrole and furan the inversion occurs between the lowest and second lowest levels more vividly than in phenol. We explain the details taking pyrrole as an example. In this case, the first excited state which is of the B_1 character in the SECI calculation turns out to be of the A_1 character in the DECI treatment. Dahl and Hansen[10] obtained by the SECI treatment the same result concerning the order of the excited levels as the present DECI calculation, adopting Nishimoto-Mataga's formula for γ_{pq} and including the penetra-

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[31] See, for example, K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965).

[*5] There is a possibility that this is due to the other effects, such as the effective σ-core change and the expansion of π-orbitals.

[32] K. Kimura, H. Tsubomura and S. Nagakura, This Bulletin, **37**, 1336 (1964).

tion integrals. Here, again, the DECI treatment shows the effect effectively similar to that of reducing γ_{pq}. In this case, however, the relative change between the two levels (1.5 eV) caused by the inclusion of the doubly excited configurations is too large to be attributed to the correlation effect. Furthermore, Chiorboli *et al.*[33] showed that, in spite of the adoptation of Nishimoto-Mataga's formula, the SECI calculation gives the order of the excited levels different from that of Dahl and Hansen when the penetration integrals are different from theirs. From these facts it is revealed that the effect of the doubly excited configurations upon the calculated energy levels is more complicated for pyrrole than for phenol and aniline.

Transition Moment. As is well known, the transition moment or oscillator strength calculated by the P-P-P method including SECI is usually too large (2—3 times) compared with the experimental value. This is corrected to a great extent by the DECI treatment. This improvement is mainly attributed to the fact that in the DECI treatment excited wavefunctions include many doubly excited configurations, the transition moments from the ground configuration to which are zero. This tendency is vivid in the transitions to higher excited levels of aniline and phenol, and the moments calculated for them are sometimes smaller than the observed values.

π-Electron Densities and Dipole Moments of Aniline. By the aid of the wavefunctions calculated by the present study, π-electron densities were evaluated for the ground state of aniline as shown in Fig. 6. This figure shows that the nonbonding electrons of the nitrogen atom migrate by 0.12—0.13 *e* toward the benzene ring and consequently the carbon atoms at the *o*- and *p*-positions turn out to have excess π-electrons by 0.08—0.09 *e* and 0.05 *e*, respectively. From these π-electron densities we calculated the dipole moment due to the π-electrons to be 1.82—1.89 D. The values are close to the π-electron moment estimated by analyzing the observed dipole moment of aniline, 1.41—1.52 D.[34,35]

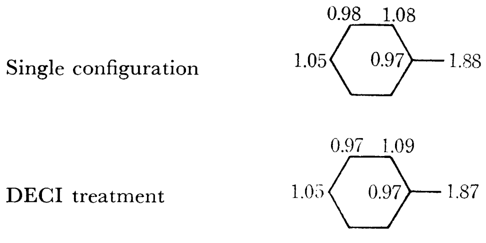

Fig. 6. Electron densities in the ground state of aniline.

The calculated π-electron densities in the first excited state of aniline are shown in Fig. 7. The corresponding quantities were estimated[36] from the analysis of the peak positions of the absorption band observed for various aminopyridines. The estimated values are also shown in Fig. 7 for the purpose of comparison, although the estimation includes much ambiguity and therefore too much importance should not be attached to them. The theoretical π-electron densities in the first excited state are qualitatively coincident with the estimated ones in the sense that excess amounts of π-electrons are located on the carbon atoms of *o*- and *m*-positions. In this connection, it may be noticed that the difference ($\Delta\mu_\pi$) in the π-electron moment between the ground and the first excited state was estimated to be ~5 D from the analysis of the solvent effect on the absorption and fluorescence spectra observed for aniline.[36] The corresponding quantity was calculated by the SECI and DECI treatment to be 1.45 D and 2.44 D, respectively. The calculated $\Delta\mu_\pi$ values are smaller than the estimated value, although the latter includes much ambiguity. From this it is revealed that the present calculation underestimates a little the π-electron migration from the nitrogen atom toward the benzene ring and therefore that a little smaller $|W_p|$ value than that in the present calculation may give better results for the π-electron distribution. Anyhow, it may be concluded from the both theoretical and experimental points of view that the π-electron migration from the nitrogen atom toward the benzene ring much increases in the first excited state compared with in the ground state.

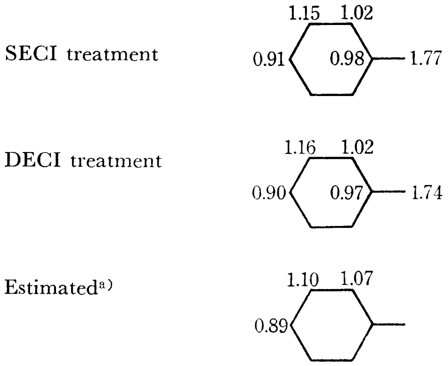

Fig. 7. Electron densities in the first excited state of aniline.

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[33] P. Chiorboli, A. Rastelli and F. Momicchioli, *Theor. Chim. Acta*, **5**, 1 (1966).

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