The Effects of Doubly-excited Configurations in the P-P-P-CI Calculation

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The effects of doubly-excited configurations, especially of the χ_{kl}^{mn} type, on the results of P-P-P-CI calculations of unsaturated compounds have been discussed by comparing the results obtained by three different types of CI treatment. The calculations of the pi-electronic total energies of ground states, the electronic transition energies, the oscillator strengths, and the pi-electronic densities of sixteen molecules were performed. The core resonance integrals and electronic repulsion integrals were readjusted so that the transition energies, obtained by CI calculations considering all the singly- and doubly-excited configurations, might coincided with the experimental results. From the results of these calculations, it is found that χ_{kl}^{mn}-type configurations play an important role in CI calculation.

Although the configuration interaction (CI) treatment considering singly-excited configurations has been investigated in detail in connection with molecular orbital (MO) calculations, few studies of the CI treatment considering doubly-excited configurations have been done.[1-6] Evleth[1] calculated transition energies by means of the P-P-P method,[7-9] the LCAO-SCF-MO method in the Pariser-Parr-Pople scheme, followed by CI treatment considering doubly-excited configurations (DEC's) under the restriction of considering only the highest two occupied levels of MO. He concluded that the DEC's are important to the calculation for transition energies which are also affected by the parameters used in the SCF-MO calculation. Allinger and Stuart[2] investigated the contribution of higher excited configurations in the CI calculations of transition energies for several unsaturated hydrocarbons. They concluded that it is not necessary to include all of the doubly-excited configurations, but it is necessary to include some triply-excited configurations, and that the higher excited configurations may be cut off at 20 eV over the ground configuration. Kashiwagi[3] calculated several electronic properties of non-alternant hydrocarbons by the P-P-P-CI method, taking account of a cut-off treatment such as has been described above. He found that the oscillator strengths and pi-electronic densities of excited states are sensitive to the introduction of DEC to the CI calculation, while transition energy to low excited states are rather insensitive, and that the introduction of DEC gives satisfactory results in the calculation of oscillator strengths. The appropriate condition of the cut-off treatment determined in his work was 13 eV. Hirota and Nagakura[4] discussed the effects of parameters and DEC's on several electronic properties calculated by the P-P-P-CI method for the molecules containing hetero-atoms. They found that the CI treatment including DEC's reduced the effect of one-center core integrals upon the calculated energy levels, and that the oscillator strengths for electronic transitions and the separations between the lowest and the second-lowest excited states were improved by this CI treatment.

The present investigation was undertaken in order to clarify the effects of DEC, especially of the χ_{kl}^{mn} type, which includes four orbitals k, l, m, and n, each containing a single electron, on the pi-electronic properties as calculated by the P-P-P-CI method for the ground and excited singlet states of unsaturated molecules. In the P-P-P-CI calculation the values of parameters, which were included in the core resonance integrals and electronic repulsion integrals, were determined so that the transition energies to some excited states might coincide with the experimental results.

Methods of Calculation

In the molecular orbital calculation of the P–P–P scheme used in this work, the core resonance integral, $\beta_{\mu\nu}$, and the two-center electronic repulsion integral, $\gamma_{\mu\nu}$, were approximated as follows:

$$\beta_{\mu\nu} = \frac{1}{2}\kappa(\beta_\mu^\circ + \beta_\nu^\circ)S_{\mu\nu} \quad (1)$$

$$\gamma_{\mu\nu} = b_{AB}/(R_{\mu\nu} + a_{AB}) \quad (2)$$

Equation (1) is the formula used in the modified CNDO method proposed by Bene and Jaffé.[10,11] Equation (2) is similar to the Mataga-Nishimoto's formula.[12] For one-center core integrals and one-center electronic repulsion integrals, the values of Table 1 in Ref. 13 were used. The parameters in these equations for carbon were readjusted so that the three transition energies of benzene (B_{2u}, B_{1u}, and E_{1u}) might coincide with the experimental values, the CI treatment in this calculation including all singly- and doubly-excited configurations. The appropriate values of these parameters were 0.645, 3.32 Å, and 35.10 Å eV for κ, a_{AB}, and b_{AB} respectively, provided that the unit of $R_{\mu\nu}$ in Eq. (2) is Å. Then, these parameter values were adopted for the calculations of all the molecules treated in this work. This value of the parameter, κ, was larger than that adjusted by the calculation including the CI treatment with singly-

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Table 1. Values of parameters in two-center electronic repulsion integrals

Pair of atoms	a_{AB}[a] (Å)	b_{AB}[a] (Å·eV)	Molecules as reference
Carbon - Carbon	3.20	35.10	Benzene
Carbon - Nitrogen	3.17	36.10	Pyridine
Nitrogen - Nitrogen	3.09	37.97	Pyrazine, Pyrimidine, and Pyridazine
Carbon - Oxygen	3.08	38.17	Phenol
Nitrogen - Oxygen	2.89	39.76	Pyridine *N*-oxide
Oxygen - Oxygen	2.87	43.68	1,4-Dioxin

a) See text.

excited configurations alone; this fact has been pointed out by other investigators as well.[5] The values of a_{AB} and b_{AB} for other pairs of atoms (C, N, and O) were determined so that the calculated values might agree very well with the observed transition energies of reference molecules. These parameter values are listed in Table 1. Before the calculation according to the parameters determined in this work were applied to several molecules, the variations in the transition energies of benzene with the change in the value of κ were discussed, the $\gamma_{\mu\nu}$ in this calculation being estimated by the Pariser-Parr approximation. Also, these transition energies obtained by calculations using the $\gamma_{\mu\nu}$ from Eq. (2) were compared with those calculated by the use of the parameters estimated by Bene and Jaffé.[10]

The configurations in CI treatments may be classified into seven basic types: χ_0, χ_k^m, χ_{kk}^{mm}, χ_{kk}^{mn}, χ_{kl}^{mm}, χ_{kl}^{mn} (1), and χ_{kl}^{mn} (2), in accordance with the Murrell and McEwen's notation.[6] χ_{kl}^{mn} (1) and χ_{kl}^{mn} (2) indicate the doubly-excited configurations which include four orbitals, k, l, m, and n, each containing a single electron; the number in parentheses is the symbol classifying the two wave functions which are eigenfunctions of the spin operator, $\mathbf{S}^2$. In order to investigate the effect of DEC on the calculated pi-electronic properties, three types of calculations were performed. They are different from each other in the point of the number of configurations included in the CI calculation. Method I includes all singly-excited configurations, while Method II includes singly- and doubly-excited configurations except for the χ_{kl}^{mn} type, and Method III, all singly- and doubly-excited configurations.

The ground-state energies, transition energies, oscillator strengths, and pi-electronic densities obtained by these three type of calculations were compared with each other for sixteen compounds. The geometries of molecules followed the data listed in Ref. 14.

Results and Discussion

Figure 1 shows the variation in the transition energies

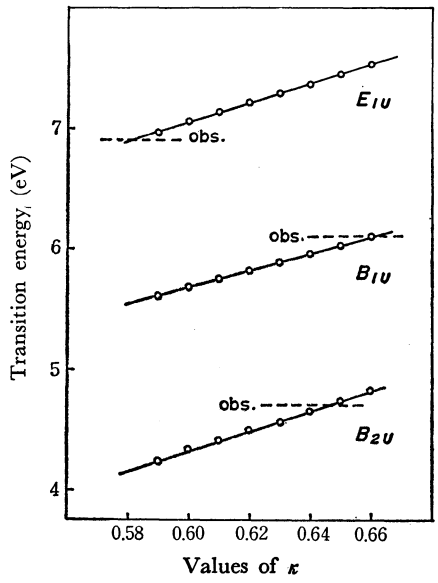

Fig. 1. The variation of transition energies of benzene with κ.

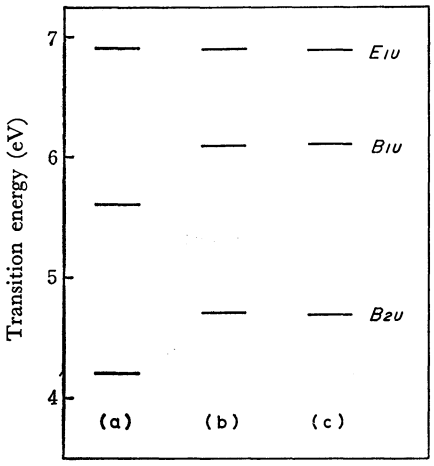

Fig. 2. Transition energies of benzene calculated by the use of different parameters.
a) Parameters are equivalent to Bene and Jaffés'.
b) Parameters were estimated by the approximation of this work.
c) observed values.

of benzene with the change in the value of κ. The transition energies increase linearly with the increased value of κ. However, the energy difference between excited states is not affected by the value of κ. In Fig. 2, the transition energies of benzene calculated by the use of the parameters estimated by Bene and Jaffé[10] are compared with the results obtained from the parameters estimated in this work. It may be seen that the energy difference between excited states of molecule is remarkably affected by the value of $\gamma_{\mu\nu}$.

In Method I, it is a matter of course that the energy of the ground state is not affected by the CI treatment considering singly-excited configurations alone. However, the ground states are stabilized by CI treatments considering singly- and doubly-excited configurations in Methods II and III, because the CI matrix elements between the ground configuration and DEC are not equal to zero. The magnitude of this stabilization

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TABLE 2. THE STABILIZATIONS OF GROUND STATE ENERGY AND THE WEIGHTS OF GROUND CONFIGURATION

Molecule	Method II		Method III	
	ΔE_0(eV)[a]	Weight	ΔE_0(eV)[a]	Weight
Benzene	0.269	0.980	0.545	0.957
trans-Butadiene	0.219	0.983	0.455	0.961
cis-Butadiene	0.206	0.985	0.451	0.962
Fulvene	0.387	0.966	0.674	0.941
Pyridine	0.252	0.982	0.519	0.961
Aniline	0.260	0.981	0.547	0.957
Pyrrole	0.295	0.978	0.465	0.962
Pyrazine	0.256	0.982	0.518	0.963
Pyrimidine	0.235	0.984	0.480	0.966
Pyridazine	0.262	0.982	0.533	0.962
s-Triazine	0.220	0.986	0.421	0.972
Phenol	0.263	0.981	0.544	0.957
Furan	0.263	0.982	0.436	0.966
1,4-Dioxin	0.211	0.986	0.515	0.957
Pyridine *N*-oxide	0.466	0.981	0.776	0.937
Pyrazine *N*-oxide	0.472	0.965	0.758	0.942

a) ΔE_0 is schematically shown in Fig. 3-a.

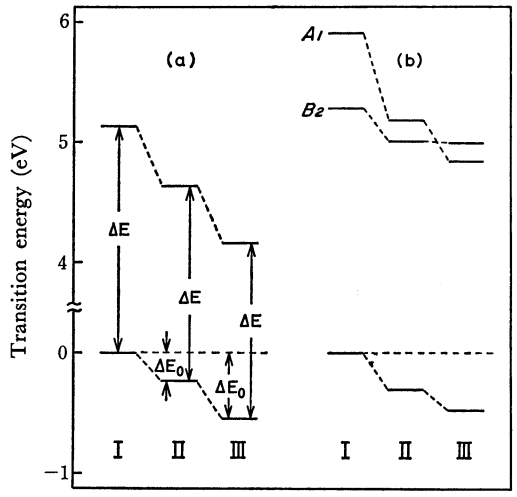

Fig. 3. Relation between energy levels calculated by different methods. (I: Method I, II: Method II, III: Method III) a) B_{2u} state of benzene b) A_1 and B_2 states of pyrrole.

energy and the contribution of the ground configuration for the ground state are listed in Table 2. From the table, it may be seen that the ground states are stabilized by from 0.20 to 0.47 eV in Method II, and by from 0.42 to 0.78 eV in Method III, and that the contributions of the ground configuration for the ground state are about 98% and 96% in Methods II and III respectively. These results show that the degree of effects of χ_{kl}^{mn}-type configurations on the results of CI calculation for the ground state is the same as that of other DEC's. The calculated transition energies and oscillator strengths are listed in Table 3, in which the experimental values are also included. In the results of Methods II and III, the transition energies are seen to depend upon the stabilization of the ground states; the energy scheme is given in Fig. 3. From Table 3 it may be found that the transition energies to low excited states calculated by Method III are in good agreement with the experimental results, and that the differences between the results from Methods I and II and between those from Methods II and III are generally less than 0.2 eV, though there are some exceptions. From these results, it is found that the degree of the effect of χ_{kl}^{mn}-type configurations on the calculated transition energies is the same as that of other DEC's. Furthermore, it is noteworthy that the energy differences between the lowest and the second-lowest excited states are improved by Method III, considering χ_{kl}^{mn}-type configurations, and that there are inversions in the order of excited levels for some molecules, as is indicated in Fig. 3-b.

The oscillator strengths calculated by Method I for the electronic transition are larger than the experimental results, but they are very much improved by Methods II and III, which consider the DEC's. From the fact that the differences between the results from Methods I and II are almost the same as those from Methods II and III, it is found that the effect of χ_{kl}^{mn}-type configurations on the oscillator strength is comparable with that of the other DEC's.

When the transition energies of molecules involving degenerate levels, such as benzene and *s*-triazine, are calculated, it should be noted that there is a defect in Method II, which considers DEC's without χ_{kl}^{mn}-type configurations, for the levels of excited states, which must be degenerate, are obtained as split levels, although the degree of splitting is very small (about 0.01 eV).

The pi-electronic densities of atomic sites in molecules varies slightly with each method of calculation. Generally, these variations in electronic densities for excited states are larger than those for the ground states of molecules. Table 4 indicates the electronic densities of fulvene and pyridazine as calculated by Methods I, II, and III. The variations between the electronic densities of these molecules calculated by the different methods are larger than those of the other molecules considered in this work. For ground states, the electron distributions in molecules were averaged by Method III as compared with other methods; the order of the magnitudes of electronic densities of the atomic sites in a molecule, except in the case of fulvene, was not affected by the method of calculation. For excited states, the calculated electron distribution did not always show the tendencies described above (see Table 4). The electronic densities of atomic sites in molecules calculated by Method III may be inferred to be reliable from the fact that the oscillator strengths are improved by this method.

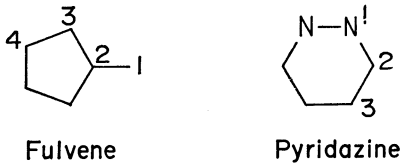

Fig. 4. Numbering of atomic sites in molecules.

TABLE 3. THE TRANSITION ENERGIES AND THE OSCILLATOR STRENGTHS

	Method I		Method II		Method III		Obsd.	
	ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)	f
Benzene								
B_{2u}	5.129	0.0	4.906	0.0	4.713	0.001	4.7	0.001[a]
B_{1u}	5.737	0.0	5.897	0.001	6.089	0.0	6.1	0.1[a]
E_{1u}	6.834	1.172	6.787	1.067	6.906	0.937	6.9	0.7[a]
trans-Butadiene								
B_u	5.816	1.032	5.919	0.871	6.155	0.765	5.9[b]	
A_g	7.065	0.0	6.404	0.0	6.275	0.0		
A_g	8.508	0.0	8.196	0.0	8.326	0.0		
cis-Butadiene								
B_2	5.322	0.400	5.448	0.360	5.693	0.316		
A_1	7.053	0.193	6.306	0.043	6.241	0.024		
A_1	8.670	0.688	8.361	0.634	8.428	0.404		
Fulvene								
B_2	3.368	0.043	3.356	0.022	3.401	0.015	3.3	0.012[c]
A_1	5.182	0.575	5.217	0.248	5.248	0.194	5.2	0.32[c]
B_2	6.659	0.202						
A_1	6.672	1.053	6.113	0.483	6.148	0.305		
B_2			6.403	0.154	6.365	0.112		
Pyridine								
B_2	5.134	0.135	4.908	0.124	4.783	0.080	4.9	0.04[d]
A_1	5.936	0.056	6.006	0.074	6.192	0.044	6.2	0.10[d]
B_2			7.012	0.289	7.070	0.337		
A_1	7.229	1.160	7.184	0.943	7.230	0.838	6.9	1.3[d]
B_2	7.280	0.928						
Aniline								
B_2	4.693	0.066	4.470	0.056	4.323	0.033	4.40	0.028[e]
A_1	5.182	0.575	5.217	0.248	5.248	0.194	5.39	0.144[e]
A_1	6.515	1.034	6.384	0.700				
B_2	6.517	0.797	6.392	0.600	6.418	0.418	6.40	0.510[e]
A_1					6.528	0.298		
Pyrrole								
A_1					5.305	0.000		
B_2	5.287	0.257	5.306	0.219	5.446	0.185	5.9[f,g]	
A_1	5.916	0.003	5.469	0.003				
A_1	7.232	0.978	7.014	0.761	7.002	0.603	6.8[f,g]	
Pyrazine								
B_{2u}	4.809	0.274	4.609	0.249	4.552	0.183	4.8	0.10[a]
B_{1u}	6.050	0.126	6.103	0.146	6.323	0.134	6.3	0.145[a]
B_{1u}	7.699	1.135	7.664	0.983	7.729	0.897	7.5	1.0[a]
Pyrimidine								
B_2	5.393	0.152	5.130	0.148	5.032	0.096	5.0	0.052[a]
A_1	6.219	0.123	6.282	0.110	6.340	0.106	6.5	0.16[a]
A_1	7.427	0.861	7.224	0.633	7.275	0.467	7.4	1.0[a]
B_2	7.731	1.053	7.608	0.890	7.614	0.736		
Pyridazine								
A_1	5.374	0.102	5.150	0.079	5.021	0.050	4.9	0.02[a]
B_2	6.084	0.002	6.138	0.017	6.321	0.007	6.2	0.10[a]
B_2	7.127	1.084	7.055	0.952	7.140	0.855	7.1	1.0[a]
A_1	7.577	1.131	7.451	0.932	7.510	0.763		
s-Triazine								
A_2'	6.065	0.0	5.866	0.004	5.650	0.0	5.6[h]	
A_1'	6.970	0.0	6.921	0.000	6.928	0.0	6.9[i]	
E'	7.665	1.025	7.465	0.828	7.476	0.725		
Phenol								
B_2	4.833	0.063	4.604	0.060	4.452	0.037	4.6	0.02[e]

TABLE 3. (Continued)

	Method I		Method II		Method III		Obsd.	
	ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)	f
A_1	5.445	0.084	5.569	0.086	5.699	0.112	5.8	0.132[e]
B_2					6.655	0.607		
A_1	6.647	1.177	6.535	0.908	6.691	0.694	6.7	0.636[e]
B_2	6.686	0.980	6.597	0.801				
Furan								
A_1					5.586	0.013		
B_2	5.375	0.252	5.449	0.226	5.625	0.200	5.8[g]	
A_1	6.169	0.066	5.706	0.036				
A_1	7.835	0.991	7.753	0.873	7.763	0.700	7.4[g]	
B_2	8.201	0.205	8.205	0.207	8.242	0.175		
1,4-Dioxin								
B_{3g}	4.244	0.0	4.453	0.0	4.555	0.0	4.7[j]	
B_{1u}	5.830	0.284	5.850	0.247	6.094	0.207	6.2[j]	
B_{3g}			7.203	0.0	6.645	0.0		
B_{1u}	7.371	1.047	7.529	0.905	7.831	0.713		
B_{3g}	7.620	0.0						
Pyridine *N*-oxide								
B_2	4.229	0.026	3.816	0.017	3.723	0.002	3.8	0.016[k]
A_1	4.401	0.401	4.321	0.364	4.360	0.365	4.4	0.205[k]
B_2	5.748	0.568	5.634	0.418	5.651	0.299	5.7	0.196[k]
A_1	6.314	0.628						
A_1			5.809	0.002	5.709	0.005		
Pyrazine *N*-oxide								
B_2			4.127	0.041	4.004	0.025		
A_1	4.484	0.444	4.315	0.400	4.322	0.399	4.52	0.186[l]
B_2	4.526	0.042						
B_2	5.656	0.504	5.389	0.385	5.443	0.272		

a) J. E. Perkin and K. K. Innes, *J. Mol. Spectrosc.*, **15**, 407 (1965). b) R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1942). c) J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, 177 (1956). d) R. L. Flurry, E. W. Stout, and J. J. Bell, *Theoret. Chim. Acta* (Berl.), **8**, 203 (1967). e) K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965). f) L. W. Pickett, N. E. Corning, G. W. Wieder, D. A. Semenow, and J. M. Buckley, *J. Amer. Chem. Soc.*, **75**, 1618 (1953). g) J. C. Tai and N. L. Allinger, *Theoret. Chim. Acta*, **15**, 133 (1969). h) R. C. Hirt, F. Halverson, and R. G. Schmitt, *J. Chem. Phys.*, **22**, 1148 (1954). i) J. C. Brinen, R. C. Hirt, and R. G. Schmitt, *Spectrochim. Acta*, **18**, 863 (1962). j) L. W. Pickett and E. Sheffield, *J. Amer. Chem. Soc.*, **68**, 216 (1946). k) M. Yamakawa, T. Kubota, and H. Akazawa, *Theoret. Chim. Acta*, **15**, 244 (1969). l) T. Kubota, This Bulletin, **35**, 946 (1962).

TABLE 4. THE PI-ELECTRONIC DENSITIES[a]

Atomic sites[b]	Ground State			1st Excited State			2nd Excited State			3rd Excited State		
	I[c]	II[c]	III[c]	I[c]	II[c]	III[c]	I[c]	II[c]	III[c]	I[c]	II[c]	III[c]
Fulvene				(ΔE=3.401 eV)			(ΔE=5.248 eV)			(ΔE=6.148 eV)		
1	0.949	0.956	0.965	1.347	1.119	1.153	0.885	0.938	0.875	0.957	1.081	1.106
2	0.955	0.950	0.952	1.078	1.180	1.154	0.798	0.876	0.893	0.942	0.760	0.765
3	1.047	1.047	1.042	0.828	0.838	0.825	1.164	1.104	1.116	0.907	1.082	1.068
4	1.001	1.000	0.999	0.959	1.013	1.022	0.994	0.990	1.000	1.143	0.998	0.996
Pyridazine				(ΔE=5.021 eV)			(ΔE=6.321 eV)			(ΔE=7.140 eV)		
1	1.134	1.135	1.130	1.194	1.154	1.135	1.135	1.185	1.184	1.140	1.151	1.158
2	0.908	0.907	0.911	0.760	0.814	0.846	0.931	0.912	0.921	0.932	0.910	0.898
3	0.957	0.958	0.959	1.046	1.032	1.019	0.934	0.907	0.895	0.927	0.938	0.944

a) ΔE is the transition energy obtained by Method III. b) Numbering of atomic sites is shown in Fig. 4. c) I, II, and III indicate Methods I, II, and III, respectively.

Conclusion

In the P-P-P-CI calculation considering the doubly-excited configurations, the effects of the κ parameter, referring to the resonance integral, β, and of the two-center electronic repulsion integral, $\gamma_{\mu\nu}$, on the transition energies of benzene were discussed. Also these parameters were readjusted so that the transition energies might coincide with the experimental results. The energy difference between the excited states of a molecule was affected remarkably by the value of $\gamma_{\mu\nu}$. By comparing the results from the three different types of calculations, which are different from each other in the point of the number of configuration included in the CI calculation, it is found that the introduction of the doubly-excited configurations to the CI treatment is effective in calculating the pi-electronic properties and that the effects of χ_{kl}^{mn}-type configurations on the results are the same as those of other doubly-excited configurations.

In these calculations, we were helped by "The University Contribution" of UNIVAC Japan, Ltd.