An Application of RPA Theory to Conjugated Systems in the Excited States

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RPA theory has been applied to the calculations of the electronic spectra of some conjugated systems, considering only π-electrons explicitly. Electron repulsion integrals have been calculated using Slater AO's with appropriate orbital exponents. The present calculation shows that the correlation effect between π-electrons is rather small for the lowest $\pi - \pi^*$ transitions. Good results have been obtained, when we calculate the electron repulsion integrals using orbital exponents evaluated by Slater rule. "Effective" electron interaction in the excited states has been discussed, using the calculated results. The calculated oscillator strengths were considerably improved by RPA.

Die RPA wurde auf die Berechnung der UV-Spektren des π-Elektronensystems konjugierter Moleküle angewendet, wobei die Coulombintegrale für Slaterorbitate mit Exponenten gemäß der Slaterregeln ermittelt wurden. Es zeigt sich, daß die Korrelationseffekte für die tieferen Übergänge ziemlich gering sind und daß sich insbesondere die Oszillatorenstärken sehr gut ergeben. Schließlich wurden eine effektive Elektronenwechselwirkung in angeregten Zuständen diskutiert.

La théorie RPA fondée sur l'équation du mouvement a été appliquée à des calculs de la structure électronique et des spectres de systèmes conjugués en ne considérant explicitement que les électrons π. Les intégrales de répulsion électronique ont été calculées en utilisant des OA de Slater avec des exposants orbitaux appropriés. Nos calculs montrent que les effets de corrélation entre électrons π sont plutôt faibles pour les plus basses transitions $\pi - \pi^*$. De bons résultats ont été obtenus en calculant les intégrales de répulsion électronique en utilisant les exposants orbitaux évalués par la règle de Slater. L'interaction électronique «effective» dans les états excités est discutée sur la base des résultats obtenus.

1. Introduction

Electron correlation must be very important in many electron systems. It is well known in many body technique [1] that electron correlation can be treated by RPA (random phase approximation) and ladder approximation methods. For high density electron systems, such as atoms and molecules, we can, however, neglect ladder diagrams [1]. In order to clarify the electron correlation, Gutfreund and Little [2, 3] calculated the screened potential in the π-electron systems by means of RPA method. Their theory leads to some interesting results. However, their theory includes an ambiguity in the calculation of effective interaction between excited configurations. In this paper, we use another RPA formula, which was recently derived by Dunning and McKoy [4] from the equations of motion method for the non-empirical calculation of excited molecules [1]. The RPA is a low-order approximation to the equations of motion, however it calculates directly the excitation energies. This method is applied to the calculations of

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[1] The same RPA equation was derived by McLachlan and Ball from the time-dependent Hartree-Fock theory [Rev. mod. Physics **36**, 844 (1964)].

the electronic spectra of benzene, benzene-N-heterocycles, and naphthalene, using ZDO (zero differential overlap) approximation. In the present method, only the correlation effect of π-electrons on the $\pi - \pi^*$ transitions is considered. Namely, the ground state electronic structure of the molecule is assumed to be unchanged.

2. Method

RPA equation can be derived from either of the following theories;
1. Time-dependent Hartree-Fock theory
2. The particle-hole Green's function method
3. Equations of motion method.

Starting from the equations of motion, a RPA equation was derived by the following manner [4]; the total Hamiltonian may be written as, in atomic units,

$$H = \sum_i \left[(-1/2)\, \Delta_i - \left(\sum_\alpha Z_\alpha / r_{\alpha i} \right) \right] + (1/2) \sum_i \sum_j (1/r_{ij})$$
$$= \sum_i H_i + (1/2) \sum_i \sum_j v_{ij}. \tag{1}$$

In the Hartree-Fock approximation, we replace the electron interaction term by an effective one particle potential V_i. Therefore, Eq. (1) can be expressed as,

$$H = \sum_i (H_i + V_i) + \sum_i \left((1/2) \sum_j v_{ij} - V_i \right). \tag{2}$$

SCF MO is the eigenfunction of the following Hartree-Fock equation

$$(H + V)|i\rangle = \varepsilon_i |i\rangle. \tag{3}$$

In the notation of second quantization, Eq. (2) is represented by

$$H = \sum_i \varepsilon_i a_i^+ a_i + (1/2) \sum_{ijkl} V_{ijkl} a_j^+ a_i^+ a_k a_l - \sum_{jk\beta} (V_{\beta j\beta k} - V_{\beta jk\beta}) a_j^+ a_k. \tag{4}$$

The operators a_i^+ and a_i are the creation and annihilation operators. The integral V_{ijkl} is defined by

$$V_{ijkl} = \int \psi_i^*(1)\, \psi_j^*(2)\, (1/r_{12})\, \psi_k(1)\, \psi_l(2)\, d\tau.$$

The ψ_i denotes the molecular spin orbital. In this equation and the ones to follow, we denote by the subscripts

$\alpha,\beta,\gamma,\delta$ ... single particle states occupied in the Hartree-Fock ground state (i.e., hole states)

m,n,p,q ... single particle states unoccupied in the Hartree-Fock ground state (i.e., particle states)

i,j,k,l ... any states (either particle or hole).

Let us define an excitation operator $A^+(E)$. This operator generates an excited state $|E\rangle$, of the Hamiltonian H, with excitation energy ΔE, when it operates on the ground state $|0\rangle$, i.e.,

$$A^+(E)\,|0\rangle = |E\rangle. \tag{5}$$

The problem is to solve the following equation of motion

$$[H, A^+(E)] \, |0\rangle = \Delta E \, A^+(E) \, |0\rangle \, . \tag{6}$$

Using the commutation rules for a_i^+, a_i, Eq. (6) can be easily rewritten as

$$(E - E_0) \, \langle 0| \, [A(E), a_m^+ a_\alpha] \, |0\rangle - \langle 0| \, \{A(E), [H, a_m^+ a_\alpha]\} \, |0\rangle = 0 \tag{7}$$

$$\begin{aligned}
[H, a_m^+ a_\alpha] = {}&(\varepsilon_m - \varepsilon_\alpha + V_{m\alpha\alpha m} - V_{m\alpha m\alpha}) \, a_m^+ a_\alpha \\
&+ \sum_{(n\beta)}' (V_{\alpha n m\beta} - V_{\alpha n \beta m}) \, a_m^+ a_\beta + \sum_{(n\beta)} (V_{\alpha\beta m n} - V_{\alpha\beta n m}) \, a_\beta^+ a_m \, .
\end{aligned} \tag{8}$$

In RPA theory, we must consider de-excitation processes, $a_\alpha^+ a_m$, in addition to the usual singly excitation processes, $a_m^+ a_\alpha$. This means that RPA theory takes the doubly excited configurations included in the true ground state into consideration. Therefore, a better approximation to excitation operator, $S^+(E)$, would be

$$S^+(E) = \sum_{(m\alpha)} [g(m\alpha:E) \, a_m^+ a_\alpha - h(m\alpha:E) \, a_\alpha^+ a_m] \, . \tag{9}$$

Using Eq. (9), Eq. (7) becomes

$$(E - E_0) \, \langle 0| \, [S(E), a_m^+ a_\alpha] \, |0\rangle - \langle 0| \, \{S(E), [H, a_m^+ a_\alpha]\} \, |0\rangle = 0 \, . \tag{10}$$

Using the commutators for a_i^+, a_i we get the set of equations from which the eigenfunctions for excited states and the corresponding excitation energies can be obtained,

$$\begin{aligned}
(\varepsilon_m - \varepsilon_\alpha &+ V_{m\alpha\alpha m} - V_{m\alpha m\alpha} - (E - E_0)] \, g(m\alpha) \\
&+ \sum_{(n\beta)}' (V_{\alpha n m\beta} - V_{\alpha n \beta m}) \, g(n\beta) + \sum_{(n\beta)} (V_{\alpha\beta m n} - V_{\alpha\beta n m}) \, h(n\beta) = 0,
\end{aligned} \tag{11}$$

where $g(m\alpha)$ and $h(n\beta)$ are the coefficients to be determined. In the present calculation, ZDO (zero differential overlap) approximation is used.

For the RPA, the transition moment is

$$^1D_{\text{RPA}} = -\sqrt{2} \, \Sigma(g(m\alpha) + h(m\alpha)) \, d_{m\alpha} \, ,$$

where

$$d_{m\alpha} = \int \psi_m^*(1) \, r \psi_\alpha(1) \, d\tau \, .$$

The oscillator strength f is defined by

$$f = 0.0875 \times \Delta E \times |D|^2 \, , \tag{12}$$

where ΔE is the calculated excitation energy in unit of eV.

For the evaluation of electron repulsion integrals, many approximations have been proposed [5]. In the present study, we would like to elucidate the correlation effect between π-electrons by RPA. For this purpose, it may be better to calculate the electron repulsion integral,

$$\gamma_{\mu\nu} = \int \varphi_\mu^2(1) \, (1/r_{12}) \, \varphi_\nu^2(2) \, d\tau ,$$

where φ_μ is the $2p\pi$ AO associated with μ-th atom, by the theoretical procedure than the semi-empirical estimation. Thus, we calculate $\gamma_{\mu\nu}$ using Slater AO's [6] with appropriate orbital exponents, ζ.

ζ's are estimated by the following three ways;

Case 1. ζ is calculated by the Slater rule [6], i.e., 1.625 for carbon and 1.95 for nitrogen.

Case 2. For one center integral $\gamma_{\mu\mu}$, ζ_μ is estimated as to reproduce the value of Pariser-Parr approximation [7],

$$\gamma_{\mu\mu} = I_\mu - A_\mu \,.$$

For the calculation of two center $\gamma_{\mu\nu}$'s, the values of ζ's are assumed to be same with the Case 1. It will be able to take some part of correlation effect by semi-empirical or empirical estimations of basic integrals over AO's into consideration. Pariser and Parr [7] estimated the $\gamma_{\mu\mu}$'s semi-empirically, and the two center $\gamma_{\mu\nu}$'s in the range of distance of $2.8\,A \geqq r > 0A$ by a empirical quadratic equation. In order to examine the effect of electron correlation in atoms on the molecular electronic spectra, we calculate one center $\gamma_{\mu\mu}$'s by semi-empirical procedure by this case.

Case 3. ζ's are estimated by Pariser-Parr approximation. They can be obtained by a relation

$$\zeta_\mu = \frac{(I_\mu - A_\mu)\,(\text{in eV})}{10.648} \,.$$

Calculated ζ's are 1.045 for carbon and 1.159 for nitrogen, respectively. Slater rule was proposed for the semi-quantitative explanation of atomic spectra [6]. There is no valence state in a free atom. Therefore, it will be, to a first approximation, able to assign same value of ζ for ns and np AO's. In a molecule, each atoms would be in an appropriate hybridization state, so that ζ for a $2p\pi$ AO may differ from that for a σ-type AO. When we assume that we can estimate a proper ζ for $2p\pi$ AO by Pariser-Parr approximation, it is reasonable to use such ζ's for the calculation of all $\gamma_{\mu\nu}$'s.

For the valence state energies, we used the experimental values given by Hinze and Jaffe [8]. That is, $2p\pi$ ionization potentials are 11.16 eV for carbon and 14.12 eV for nitrogen, respectively. The values of valence state electron affinities are 0.03 eV for carbon and 1.78 eV for nitrogen, respectively.

For a simplicity, all of two center core integrals,

$$\beta_{\mu\nu} = \int \varphi_\mu(1)\, H_{\text{core}}\, \varphi_\nu(1)\, d\tau \,,$$

and bond distances are assumed to be -2.4 eV and 1.4 Å.

The procedure of calculation is as follows; Firstly, we calculate SCF MO's by conventional Hartree-Fock scheme using ZDO approximation. Secondly, we construct all possible singly excited configurations. The excited state of molecule can be expressed by the linear combinations of these configurations. So that, we must diagonalize the configuration interaction matrix of m order and then obtain the excited state energies and state functions by this procedure. In the Tables, we denote this type calculation by SECI (singly excited configuration interaction). Thirdly, we may perform the RPA calculation considering the same number of de-excitation processes. Therefore, RPA matrix to be solved in the present calculation should be $2m \times 2m$ in dimension.

RPA matrix is usually not Hermite, so that the coefficients in Eq. (11), $g(m\alpha)$ and $h(m\alpha)$'s, have to be normalized differently, by the following relation,

$$\Sigma[g(m\alpha; E)\, g(m\alpha; E') - h(m\alpha; E)\, h(m\alpha; E')] = \pm\, \delta_{EE'}, \qquad (13)$$

where $g(m\alpha; E)$ and $h(m\alpha; E)$ mean the coefficients associated with an excited state $|E\rangle$.

3. Results and Discussion

One of the most important problems in the calculation of electronic spectra of a molecule is the estimation of electron repulsion integrals. In Table 1, $\gamma_{\mu\nu}$'s calculated by various approximations are summarized. It is interesting to note that the values of $\gamma_{\mu\nu}$'s of Case 3 are rather close to those of Pariser's, except only γ_{12}.
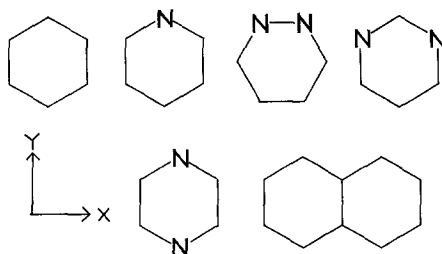

Fig. 1. Molecular frameworks

Table 1. Calculated electron repulsion integrals for benzene (in eV)

Distance (in Å)	Case 1	Case 2	Case 3	Pariser[a]	Nishimoto-Mataga[b]
0	17.277	(11.13)	(11.13)	10.959	(11.13)
1.4	9.040	9.040	7.770	6.895	5.345
2.425	5.655	5.655	5.332	5.682	3.872
2.8	4.953	4.953	4.730	4.978	3.517

[a] Ref. [9].
[b] Ref. [10].

Electronic Spectra

Calculated results for singlet $\pi - \pi^*$ transitions are summarized in Tables 2, 3, and 4. As seen from these Tables, RPA theory based on Case 1 calculates excellent results of transition energies from the ground state to the two lowest excited states of benzene and benzene-N-heterocycles. Furthermore, the calculated oscillator strength is remarkably improved by RPA method. Namely, usual SECI theory calculates almost of twice value compared with observed ones, whereas RPA theory calculates the oscillator strengths very close to experimental values. This great deduction of oscillator strength by RPA is due to a contribution of de-excitation processes which correspond to the de-excitation of the doubly excited components of the true ground state.

Table 2. Transition energies (ΔE in eV) and intensities (f) of benzene[a]

State	Case 1		Case 2		Case 3		Obs.	Ref.
	SECI	RPA	SECI	RPA	SECI	RPA		
$^1B_{2u}$	5.13(0)	4.84(0)	5.13(0)	4.84(0)	5.01(0)	4.86(0)	4.9 (−)	[11]
$^1B_{1u}$	6.16(0)	6.10(0)	3.51(0)	2.82(0)	4.82(0)	4.77(0)	6.07(.1)	[12]
	13.42(0)	13.36(0)	12.96(0)	12.96(0)	12.14(0)	12.14(0)		
$^1E_{1u}$	9.11(3.125)	8.03(1.450)	8.08(2.771)	7.38(1.548)	7.48(2.567)	6.99(1.537)	6.95	[12]
$^1E_{2g}$	10.04(0)	9.63(0)	7.98(0)	7.94(0)	8.31(0)	8.23(0)		
	10.26(0)	10.25(0)	10.26(0)	10.25(0)	9.43(0)	9.43(0)		

[a] The oscillator strengths are given in brackets.

Table 3. Transition energies (ΔE in eV) and intensities (f) of benzene N-heterocycles

State	Case 1		Case 2		Case 3		Obs.	Ref.
	SECI	RPA	SECI	RPA	SECI	RPA		
			Pyridine					
$^1B_2$	5.14(0.005)	4.85(0.004)	5.26(0.067)	5.05(0.059)	4.94(0.072)	4.80(0.063)	4.9 (−)	[11]
	9.13(1.552)	8.05(0.719)	8.03(0.449)	7.70(0.618)	7.53(1.135)	7.11(0.689)	7.22 (−)	[12]
	10.01(0)	9.63(0)	8.37(0.650)	8.20(0.084)	8.36(0.002)	8.28(0.001)		
	10.32(0.004)	10.29(0.001)	10.59(0.008)	10.58(0.009)	9.48(0.018)	9.47(0.010)		
$^1A_1$	6.32(0.005)	6.24(0.004)	4.33(0.002)	3.96(0.002)	5.15(0.002)	5.12(0.002)	6.17(0.2)	[12]
	9.25(1.465)	8.15(0.709)	7.96(0.922)	7.51(0.741)	7.46(1.206)	7.01(0.754)	7.22(−)	[12]
	10.31(0.054)	9.89(0.010)	8.48(0.301)	8.37(0.049)	8.47(0.042)	8.37(0.011)		
	10.50(0.066)	10.34(0)	10.81(0.002)	10.80(0)	9.58(0.002)	9.57(0.001)		
	13.53(0.002)	13.45(0)	13.25(0)	13.25(0)	12.23(0)	12.23(0)		
			Pyridazine					
$^1A_1$	5.15(0.004)	4.85(0.004)	5.03(0.060)	4.73(0.050)	4.94(0.055)	4.78(0.049)	5.00(−)	[11]
	9.38(1.451)	8.22(0.704)	8.07(0.296)	7.60(0.655)	7.64(1.169)	7.16(0.699)	7.32(0.5)	[13]
	10.19(0.044)	9.78(0.008)	8.43(1.024)	8.13(0.041)	8.50(0.029)	8.41(0.005)		
	10.48(0.119)	10.36(0.005)	10.57(0.025)	10.55(0.008)	9.69(0.039)	9.66(0.014)		
$^1B_2$	6.45(0.004)	6.36(0.004)	3.65(0)	3.05(0)	5.03(0)	5.00(0)	6.39(0.1)	[13]
	9.18(1.500)	8.08(0.711)	7.91(0.705)	7.35(0.703)	7.39(1.212)	6.91(0.745)	7.32(0.5)	[13]
	10.35(0.034)	10.02(0.007)	8.28(0.652)	8.09(0.042)	8.43(0.040)	8.33(0.010)		
	10.63(0.047)	10.35(0.002)	10.26(0.018)	10.25(0.006)	9.44(0.017)	9.43(0.008)		
	13.66(0.002)	13.56(0)	13.36(0)	13.36(0)	12.45(0)	12.45(0)		
			Pyrimidine					
$^1B_2$	5.15(0.005)	4.86(0.004)	5.73(0.083)	5.60(0.074)	5.09(0.076)	4.96(0.067)	5.16(−)	[11]
	9.30(1.413)	8.21(0.701)	8.34(0.813)	8.05(0.624)	7.71(1.089)	7.32(0.686)	7.40(0.5)	[13]
	10.38(0.041)	10.03(0.016)	8.93(0.133)	8.87(0.040)	8.62(0.036)	8.54(0.009)		
	10.71(0.142)	10.41(0)	11.57(0)	11.57(0.001)	9.91(0)	9.91(0)		
$^1A_1$	6.52(0.006)	6.42(0.006)	5.47(0.006)	5.30(0.006)	5.41(0.005)	5.39(0.005)	6.42(0.16)	[13]
	9.22(1.522)	8.11(0.712)	8.25(0.870)	7.97(0.671)	7.51(1.117)	7.12(0.724)	7.40(0.5)	
	10.17(0.030)	9.76(0.003)	8.60(0.072)	8.56(0.019)	8.45(0.003)	8.38(0.001)		
	10.41(0.003)	10.34(0.001)	11.03(0.008)	11.03(0.010)	9.61(0.015)	9.60(0.012)		
	13.61(0.001)	13.52(0)	13.47(0.001)	13.47(0.001)	12.34(0)	12.34(0)		

Table 3 (Continued)

State	Case 1		Case 2		Case 3		Obs.	Ref.
	SECI	RPA	SECI	RPA	SECI	RPA		
			Pyrazine					
$^1B_{1u}$	5.13(0.020)	4.82(0.018)	4.84(0.219)	4.50(0.165)	4.71(0.217)	4.50(0.172)	4.77(−)	[11]
	9.20(1.557)	8.10(0.707)	8.73(1.168)	8.11(0.581)	7.98(1.063)	7.56(0.595)	7.65(0.5)	[13]
$^1B_{2u}$	6.47(0.021)	6.37(0.020)	3.73(0.003)	3.16(0.003)	5.10(0.010)	5.07(0.010)	6.33(0.145)	[13]
	9.59(1.593)	8.34(0.695)	8.28(1.350)	7.57(0.733)	7.66(1.240)	7.17(0.744)	7.65(0.5)	[13]
	13.62(0.006)	13.53(0)	13.26(0)	13.26(0)	12.32(0)	12.31(0)		
$^1B_{3g}$	9.92(0)	9.58(0)	7.81(0)	7.78(0)	8.13(0)	8.06(0)		
	10.44(0)	10.37(0)	10.62(0)	10.61(0)	9.76(0)	9.75(0)		
$^1A_{1g}$	10.29(0)	10.01(0)	8.09(0)	8.04(0)	8.32(0)	8.24(0)		
	10.84(0)	10.53(0)	10.89(0)	10.89(0)	10.01(0)	9.99(0)		

Table 4. Transition energies and intensities of naphthalene

| State	Case 1		Case 2		Case 3		Obs.	Ref.
	SECI	RPA	SECI	RPA	SECI	RPA		
$^1B_{1u}$	4.39(0)	4.07(0)	4.39(0)	4.07(0)	4.28(0)	4.10(0)	3.97(0.002)	[14]
	7.45(2.538)	6.73(1.350)	6.87(2.563)	6.34(1.447)	6.45(2.370)	6.04(1.445)	5.63(1.70)	[14]
	9.81(0)	9.52(0.065)	8.18(0.002)	8.09(0.001)	8.23(0.044)	8.15(0.021)		
	10.04(0.314)	9.80(0)	9.81(0)	9.80(0)	9.03(0)	9.03(0)		
	11.07(0)	11.06(0)	11.07(0)	11.06(0)	10.10(0)	10.09(0)		
	11.87(0.039)	11.87(0.017)	11.86(0.023)	11.86(0.014)	10.78(0.029)	10.77(0.019)		
$^1B_{2u}$	5.00(0.100)	4.87(0.099)	2.91(0.050)	1.76(0.034)	4.00(0.107)	3.87(0.097)	4.51(0.18)	[14]
	7.73(0.523)	7.19(0.437)	7.02(0.664)	6.51(0.480)	6.61(0.676)	6.26(0.469)	6.51(0.21)	[14]
	9.64(1.518)	9.16(0.610)	8.50(0.559)	8.38(0.423)	8.43(1.032)	8.25(0.591)	7.44(0.8)	[15]
	10.79(0.243)	10.30(0.005)	9.35(0.832)	9.07(0.201)	9.13(0.178)	9.00(0.020)		
	11.10(0)	11.10(0)	11.10(0)	11.10(0)	10.27(0)	10.27(0)		
	12.56(0.034)	12.52(0.006)	12.23(0.044)	12.21(0.012)	11.41(0.022)	11.40(0.007)		
	15.95(0.002)	15.93(0.002)	15.80(0.001)	15.80(0.001)	14.56(0.002)	14.55(0.002)		
$^1A_{1g}$	6.38(0)	6.25(0)	6.38(0)	6.25(0)	6.13(0)	6.06(0)		
	8.85(0)	8.66(0)	7.25(0)	7.16(0)	7.50(0)	7.37(0)		
	8.88(0)	8.84(0)	8.85(0)	8.30(0)	8.12(0)	7.84(0)		
	10.15(0)	8.97(0)	8.92(0)	8.84(0)	8.24(0)	8.11(0)		
	12.17(0)	12.03(0)	11.60(0)	11.58(0)	10.89(0)	10.87(0)		
	13.01(0)	13.01(0)	13.01(0)	13.01(0)	11.92(0)	11.92(0)		
$^1B_{3g}$	6.97(0)	6.71(0)	4.71(0)	4.58(0)	5.45(0)	5.40(0)		
	7.35(0)	7.35(0)	7.35(0)	7.35(0)	6.72(0)	6.71(0)		
	9.30(0)	8.84(0)	8.18(0)	7.90(0)	8.88(0)	7.71(0)		
	9.81(0)	9.80(0)	9.81(0)	9.80(0)	9.05(0)	9.04(0)		
	13.23(0)	13.16(0)	12.87(0)	12.87(0)	12.02(0)	12.01(0)		
	15.20(0)	15.20(0)	15.20(0)	15.20(0)	13.85(0)	13.85(0)		
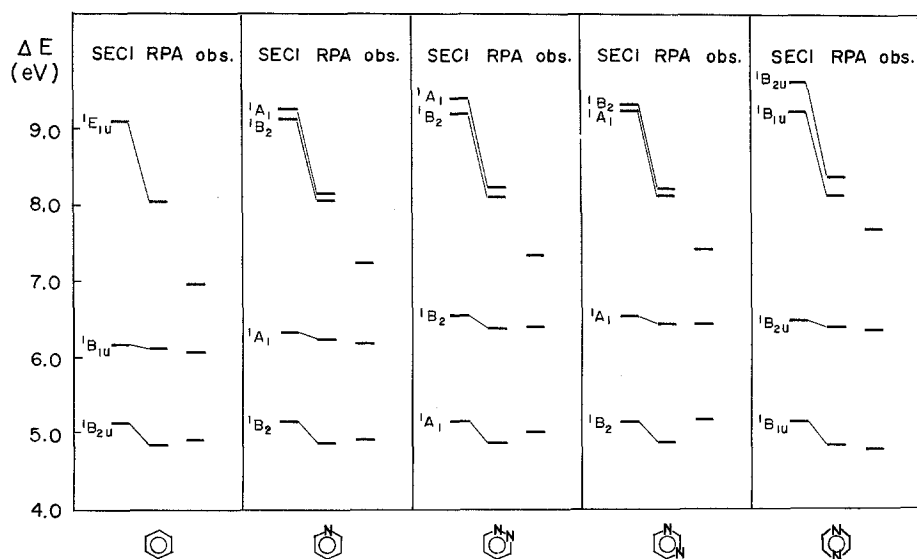
Fig. 2. Energy levels of benzene and benzene N-heterocycles (Case 1)

In the calculation of Case 2, we obtained extremely unsatisfactory results of the transition energies from the ground state to the second lowest excited states, which are polarized to the direction of molecular y axis. The reason for this may be ascribed to the fact that transition energy of $^1B_{1u}$ species is mainly determined by a difference of $(\gamma_{11} - \gamma_{12})$ (see Eq. (14)). In Case 2, $\gamma_{11} - \gamma_{12}$ is extremely small compared with other two cases.

RPA theory of Case 3 calculates rather good results for the energies of the first and third lowest excited states. However, the results for second lowest excited states are unsatisfactory.

It will be meaningful to estimate effective interactions between π-electrons in tions is generally large, whereas that of the second transitions is rather small.

Correlation Effect and "Effective" $\gamma_{\mu\nu}$'s

It will be meaningful to estimate effective interactions between π-electrons in the excited states. When we consider only four lowest singly excited configurations (4 CI) in benzene, the transition energies can be expressed as follows in ZDO approximation;

$$\Delta E(^1B_{2u}) = -2\beta + (1/6)(\ \gamma_{12} - 3\gamma_{13} + 2\gamma_{14})$$
$$\Delta E(^1B_{1u}) = -2\beta + (1/6)(2\gamma_{11} - 5\gamma_{12} + 7\gamma_{13} - 4\gamma_{14}) \tag{14}$$
$$\Delta E(^1E_{1u}) = -2\beta + (1/6)(\ \gamma_{11} + 4\gamma_{12} - 4\gamma_{13} - \ \gamma_{14})\ .$$

In the RPA calculation, we have to consider the corresponding four de-excitation processes. The calculated results based on 4 CI using $\gamma_{\mu\nu}$'s of Case 1 are given in Table 5. In this paper, we assume the transition energies of benzene calculated

Table 5. Transition energies and intensities of benzene (2)

State	Case 1	
	4 CI	RPA
$^1B_{1u}$	5.130(0)	4.843(0)
$^1B_{2u}$	6.322(0)	6.320(0)
$^1E_{1u}$	9.111(3.125)	8.026(1.450)

by RPA theory can be given by the same equations with Eq. (14) and define the corresponding $\gamma_{\mu\nu}$'s as "effective" electron repulsion integrals, $\gamma_{\mu\nu}^{\text{eff}}$'s. Then, we can easily obtain, from Table 5,

$$\gamma_{11}^{\text{eff}} - \gamma_{12}^{\text{eff}} = 6.040 \text{ eV}$$

$$\gamma_{12}^{\text{eff}} - \gamma_{13}^{\text{eff}} = 2.445 \text{ eV}$$

$$\gamma_{13}^{\text{eff}} - \gamma_{14}^{\text{eff}} = 1.093 \text{ eV} .$$

When we assign 4.953 eV for the value of γ_{14}^{eff}, we obtain

$$\gamma_{11}^{\text{eff}} = 14.531(17.277) \text{ eV}$$

$$\gamma_{12}^{\text{eff}} = 8.491(9.040) \text{ eV}$$

$$\gamma_{13}^{\text{eff}} = 6.046(5.655) \text{ eV}$$

where, for a comparison, the corresponding theoretical values are given in the brackets. That is, γ_{11} and γ_{12} are respectively decreased by 2.75 eV and 0.55 eV, whereas that of γ_{13} is increased by 0.39 eV by correlation effect at the low lying excited states. This fact indicates that there is a rather complicated many body interactions, such as induced polarization in electron cloud suggested in the previous paper [16]. The excited singlet states involve large amounts of ionic structures, in terminology of valence bond theory. Therefore, an effect of electron correlation on γ_{11} should be quite large. This may be a reason why γ_{11}^{eff} is decreased remarkably at the excited states.

In order to make further improvement of the present calculation, it should be considered the following problems; 1. The effect of $\sigma - \pi$ interactions on $\gamma_{\mu\nu}$'s must be taken into account. 2. Two center core integral $\beta_{\mu\nu}$ should be varied with the change in the interatomic distance. 3. $\gamma_{\mu\nu}$'s should be calculated using the interatomic distances in the equilibrium positions in each molecules. In the next papers, we will study the above mentioned problems.

References

1. Mattuck,R.G.: A guide to Feynman diagrams in the many body problems. New York: MacGraw-Hill
2. Gutfreund, H., Little,W.A.: Physic. Rev. **183**, 68 (1969).
3. Gutfreund, H., Little,W.A.:J. chem. Physics **50**, 4468, 4478 (1969).
4. Dunning,H.T., McKoy,V.: J. chem. Physics **47**, 1735 (1967).
5. Parr,R.G.: The quantum theory of molecular electronic structure. New York: W. A. Benjamin 1963.

6. Slater, J. C.: Physic. Rev. **36**, 51 (1930).
7. Pariser, R., Parr, R. G.: J. chem. Physic. **21**, 767 (1953).
8. Hinze, J., Jaffe, H. H.: J. Amer. chem. Soc. **84**, 540 (1962).
9. Pariser, R.: J. chem. Physics **24**, 324 (1956).
10. Nishimoto, K., Mataga, N.: Z. physik. Chem. (Frankfurt) **12**, 335 (1957).
11. Halverson, F., Hirt, R. C.: J. chem. Physics **19**, 711 (1951).
12. El-Sayed, M. A.: J. chem. Physics **36**, 552 (1962).
13. Parkin, J. E., Innes, K. K.: J. molecular Spectroscopy **15**, 407 (1965).
14. Murrell, J. N.: The theory of the electronic spectra of organic molecules. London: Methuen 1963.
15. Mann, D. E., Platt, J. R., Klevens, H. B.: J. chem. Physics **17**, 481 (1949).
16. Nishimoto, K.: Theoret. chim. Acta (Berl.) **7**, 207 (1967).

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