Theoret. chim. Acta (Berl.) 31, 91—94 (1973)

Relationes

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

II. Linear Polyenes

Kazuo Kitaura and Kichisuke Nishimoto
Department of Chemistry, Osaka City University, Sumiyoshi-Ku, Osaka, Japan

Received January 15, 1973

In order to obtain a relationship between the molecular dimension and the correlation effect, RPA method has been applied to the calculation of electronic transition energies of linear polyenes. It has been found that the effect of electron correlation on the excitation energy decreases with increasing the size of molecule. The calculated oscillator strengths are remarkably improved by RPA calculation.

Key words: RPA calculation – Conjugated systems – Polyenes – Transition energies.

The calculation of the electronic transition energy is usually carried out by considering the configuration interaction (CI) among the excited configurations. It can be assumed that the configuration of very high energy would make no significant contribution to the lower excited states. Therefore, the CI procedure is usually made among only a limited number of the lower singly excited configurations. However, in some molecules, certain lower excited states are largely affected by doubly excited configurations [1]. For large molecules, these effects are not so clear, since the number of doubly excited configurations becomes very large.

The RPA method provides a tool of studying correlation effect on the lower excited states avoiding troublesome with large CI calculation [2, 3]. The RPA method does not handle doubly excited configurations explicitly, but it takes partly into account their effects to the lower excited states as de-excitation processes of doubly excited configurations included in the ground state. Previously, Donath [4] showed that the third excited state of benzene was strongly affected by the doubly excited configurations. As we have shown in the previous paper [5], the RPA calculation gave the same result. It is interesting to know the dependence of molecular size on the correlation effect to the excitation energy, because the electron repulsion integrals over molecular orbitals (MO's) are reduced as the dimensions of MO's increase. For this purpose, the energies of $\pi-\pi^*$ transitions of linear polyenes are calculated by RPA method in this paper. The procedure of calculation and the parametrization are the same with those in our previous paper [5]. In the calculation, all of the C–C bond lengths and the bond angles were set to 1.4 Å and 120°, respectively. The two center core integral (β_{cc}) was taken to be equal to -2.2 eV for all molecules. The electron repulsion integrals were calculated using Slater type AO with appropriate orbital exponent, ζ.

As we have reported in the previous paper [5], for the RPA calculation, the orbital exponent calculated by Slater rule gave quite good results. Therefore, the same parametrization ($\zeta_c = 1.625$) is used in this paper.

The results obtained by the method of configuration interaction among all possible singly excited configurations (SECI) and the corresponding RPA calculation are shown in Tables 1, 2 and Fig. 1, together with the experimental values. In these tables, only the results for the lower excited states are given.

In order to examine the influence of molecular geometry on the correlation effect, the singlet energy levels of *cis*- and *trans*-butadienes are calculated. The results are shown in Table 1. As seen from the table, the correlation effect in the *cis*-form seems to be rather larger than that in the *trans*-form. But, the difference is quite small. It is interesting to note that the first and third energy levels of *trans*-butadiene vary to a considerable extent by the RPA method, compared with those obtained by SECI calculation. For a comparison, another value of ζ_c, which is determined as reproduce the value of Pariser-Parr approximation [6] for one center electron repulsion integral, i.e., 1.045 for carbon, is examined. The results calculated by this parameter are given in the same table. It should be noted that in this case the second transition of butadiene is rather largely varied by the mixing of de-excitation processes. Allinger [7] has reported that this transition was remarkably affected by the doubly excited configurations, when he calculated the transition energies using semi-empirical electron repulsion integrals. Namely the effect of doubly excited configurations (or de-excitation processes in the case of RPA method) depends largely on the electron repulsion integrals used, which we have already pointed out in the previous paper [5]. Semi-empirical electron repulsion integrals might already include partly a correlation effect. Therefore, when we use semi-empirical parameters, then the CI calculation including the doubly excited configurations may overestimate the correlation effect.

Table 1. Excitation energies (ΔE in eV) and oscillator strengths (in paranthesis) of *cis*- and *trans*-butadienes

Case 1[a]		Case 2[b]			
SECI	RPA	SECI	RPA	Obs	Ref.
Cis-Butadiene					
5.99 (0.503)	5.04 (0.288)	5.07 (0.463)	4.96 (0.366)	4.95[c]	[8]
7.26 (0.000)	7.22 (0.000)	7.91 (0.000)	7.89 (0.000)		
9.71 (1.114)	8.29 (0.534)	8.41 (0.933)	8.07 (0.669)		
9.78 (0.006)	9.62 (0.015)	10.41 (0.048)	10.38 (0.036)		
Trans-Butadiene					
6.44 (1.242)	5.71 (0.704)	5.53 (1.210)	5.36 (0.915)	5.71	[9]
7.50 (0.000)	7.48 (0.000)	7.93 (0.000)	7.68 (0.000)		
9.21 (0.000)	7.98 (0.000)	8.10 (0.000)	8.09 (0.000)		
10.06 (0.264)	9.86 (0.130)	10.64 (0.164)	10.62 (0.153)		

[a] $\zeta_c = 1.625$ and $\beta_{cc} = -2.2$ eV.

[b] $\zeta_c = 1.045$ and $\beta_{cc} = -2.8$ eV.

[c] The value of cyclohexadiene.

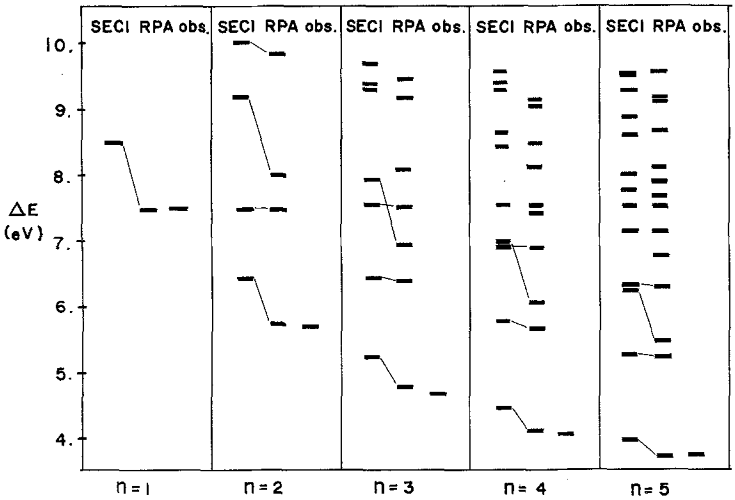

Fig. 1. Correlation diagram of excitation energies of linear polyenes

Table 2 and Fig. 1 show the lower singlet excitation energies and the oscillator strengths of linear polyenes calculated by the RPA and the SECI methods. The lowest excitation energies of small molecules are considerably lowered by the RPA treatment. However, as the size of molecule becomes larger, this effect becomes of little importance. This result shows that the correlation energy of the lowest excited state of large molecule cancels with that of the ground state within the RPA method. The reason for this may be due to a fact that an increase of the content of ionic structure (in terms of the terminology in valence bond theory) by an excitation becomes smaller as the dimension of MO becomes larger. It is evident that the electron correlation brings always to decrease such ionic structures.

As seen from Table 2, the calculated oscillator strengths are remarkably improved by RPA treatment. For example, f of *trans*-butadiene decreases from 1.242 to 0.704 which is very close to the experimental value ($f=0.53$). It might be meaningful to estimate effective interactions between π-electrons in the excited states. The transition energy of ethylene can be expressed as follows in ZDO approximation;

$$\Delta E = -2\beta + (1/2)(\gamma_{11} - \gamma_{12}) \, .$$

where $\gamma_{\mu\nu}$ means the electron repulsion integral associated with $2p\pi$ AO's, ϕ_μ and φ_ν. When we assume that the transition energy of ethylene calculated by the RPA method can be given by the same expression and we define the corresponding $\gamma_{\mu\nu}$'s as "effective" electron repulsion integrals, $\gamma_{\mu\nu}^{\text{eff}}$'s, then we obtain

$$\gamma_{11}^{\text{eff}} - \gamma_{12}^{\text{eff}} = 6.117 \text{ eV} \, .$$

In benzene, this quantity was to be 6.040 eV. It should be noted that this value is almost the same as the value calculated by our semi-empirical formula [12].

Table 2. Energies (ΔE in eV) and oscillator strengths (in paranthesis) of the lower excited states of linear polyenes; H–(CH=CH)$_n$–H

SECI	RPA	Obs.	Ref.
	$n = 1$		
8.52 (0.730)	7.46 (0.377)	7.47	[10]
	$n = 2$		
6.44 (1.242)	5.71 (0.704)	5.71	[9]
7.50 (0.000)	7.48 (0.000)		
9.21 (0.000)	7.98 (0.000)		
10.06 (0.264)	9.86 (0.130)		
	$n = 3$		
5.27 (1.706)	4.78 (1.009)	4.71	[11]
6.47 (0.000)	6.43 (0.000)		
7.55 (0.000)	6.96 (0.000)		
7.95 (0.000)	7.54 (0.000)		
	$n = 4$		
4.52 (2.124)	4.16 (1.312)	4.15	[11]
5.77 (0.000)	5.72 (0.000)		
6.93 (0.000)	6.14 (0.000)		
7.01 (0.000)	6.90 (0.000)		
	$n = 5$		
4.02 (2.497)	3.74 (1.613)	3.80	[11]
5.31 (0.000)	5.24 (0.000)		
6.27 (0.000)	5.50 (0.000)		
6.36 (0.000)	6.33 (0.000)		

References

1. Hirota, F., Nagakura, S.: Bull. Chem. Soc. Japan **43**, 1010 (1970)
2. Dunning, H. T., McKoy, V.: J. Chem. Phys. **47**, 1735 (1967)
3. McLachlan, A. D., Ball, M. A.: Rev. Mod. Phys. **36**, 844 (1964)
4. Donath, W. E.: J. Chem. Phys. **40**, 77 (1964)
5. Kitaura, K., Nishimoto, K.: Theor. Chim. Acta (Berl.) (in press)
6. Pariser, R., Parr, R. G.: J. Chem. Phys. **21**, 767 (1953)
7. Allinger, N. L., Tai, J. C.: J. Amer. Chem. Soc. **87**, 2081 (1965)
8. Schuler, H., Lutz, E., Arnold, G.: Spectrochim. Acta **17**, 1043 (1961)
9. Kiersteard, R. W., Linstead, R. P., Weeden, B. C. L.: J. Chem. Soc. 1803 (**1953**)
10. Wilkinson, P. G., Johnston, H. L.: J. Chem. Phys. **18**, 190 (1950)
11. Bohlmann, F., Mannhardt, H.: Chem. Ber. **89**, 1307 (1956)
12. Nishimoto, K., Mataga, N.: Z. Physik. Chem. (Frankfurt) **12**, 335 (1957)

Prof. Dr. K. Nishimoto
Department of Chemistry,
Osaka City University
Sumiyoshi-Ku, Osaka
Japan