Theoret. chim. Acta (Berl.) 5, 74—78 (1966)

An Improvement in the Calculation of Electron Repulsion Integrals in Pariser-Parr-Pople Theory — Electron Interactions in Molecules

KICHISUKE NISHIMOTO

Department of Chemistry, Faculty of Science, Osaka City University, Osaka, Japan

Received March 25, 1966

An improvement in the calculation of electron repulsion integrals in Pariser-Parr-Pople theory has been made, considering the following two characteristic features associated with electron interactions in molecules; Firstly, a given π-electron moves in the sea of electron clouds consisted of σ-electrons and other π-electrons, which forms a polarizable dielectric medium. Secondly, in alternant hydrocarbons, π-electrons will be alternatively distributed to the "upper" and "lower" sides of molecular plane. The present idea is applied to SCF MO calculations of simple hydrocarbons. Calculated results for singlet and triplet transitions energies, and first ionization potentials are in good agreement with experimental data.

Bei der Berechnung der Elektronenwechselwirkungsintegrale im Rahmen der PPP-Theorie wird eine Verbesserung angegeben, die folgende Charakteristika betrifft: 1. Ein gegebenes π-Elektron bewegt sich im Feld der übrigen σ- und π-Elektronen, die ein polarisierbares elektrisches Medium bilden; 2. in alternierenden Kohlenwasserstoffen sind die π-Elektronen abwechselnd auf der Ober- und Unterseite der Molekülebene verteilt. Diese Idee wird auf SCF MO Rechnungen von einfachen Kohlenwasserstoffen angewandt. Die Ergebnisse von Singulett- und Triplettübergangsenergien und Ionisierungspotentialen stimmen mit den experimentellen Daten gut überein.

On a amélioré le calcul des intégrales de répulsion électronique dans la théorie de Pariser-Parr-Pople en prenant en considération les deux aspects caractéristiques suivant de l'interaction électronique dans les molécules. Premièrement, un électron π donné se déplace dans la mer des nuages électroniques des électrons σ et des autres électrons π, qui forme un milieu diélectrique polarisable. Deuxièmement, dans les hydrocarbures alternants, les électrons π seront alternativement distribués sur les côtés supérieurs et inférieurs du plan moléculaire. Cette idée est appliquée à des calculs SCF MO d'hydrocarbures simples. Les résultats des calculs pour les énergies de transition singulet et triplet et pour les premiers potentiels d'ionisation sont en bon accord avec les donées expérimentales.

Introduction

The usefulness of the Pariser-Parr-Pople theory [*20, 24*] is rapidly increasing with the development of large digital computers. This theory includes two kinds of basic parameters, electron repulsion integral, $\gamma_{\mu\nu} = \int \varphi_\mu^2\,(1)\,(e^2/r_{12})\,\varphi_\nu^2\,(2)\,dv$, and core integral, $\beta_{\mu\nu} = \int \varphi_\mu\,(1)\,H_{\text{core}}\,\varphi_\nu\,(1)\,dv$, where φ_μ is the $2p\pi$ AO centered at μ-th atom. Several methods of calculating these integrals have been proposed [*16, 19, 21*]. NM approximation [*18*] for $\gamma_{\mu\nu}$ has been obtained from the following procedure; $\gamma_{\mu\nu}$ may be expressed by $\gamma_{\mu\nu} = e^2\,G\,(R_{\mu\nu})/F\,(R_{\mu\nu})$, where $G\,(R_{\mu\nu})$ and $F\,(R_{\mu\nu})$ are the some functions of interatomic distance $R_{\mu\nu}$ between μ-th and ν-th atoms. First approximation might be $\gamma_{\mu\nu} = e^2\,(R_{\mu\nu} + b)/(R_{\mu\nu}^2 + aR_{\mu\nu} + c)$, because there is a restriction that at quite large distance $\gamma_{\mu\nu} = e^2/R_{\mu\nu}$. Using three benzene singlet transition energies and Pariser-Parr approximation, $\gamma_{11} = I - A$, the coefficients were determined as $b = c = 0$ and $a = e^2/(I - A)$, or $\gamma_{\mu\nu} = e^2/(R_{\mu\nu} + a)$. This NM expression is useful for the calculations of singlet transition energies and bond lengths of various hydrocarbons and heteroatomic systems [*2*, *19*]. However, this expression is not adequate for the calculations of triplet energies. Moreover, the physical meaning of $R + a$ is not clear.

The purpose of this paper is to propose a more reasonable method for the calculation of $\gamma_{\mu\nu}$'s and to apply it to some simple hydrocarbons.

Method

In order to improve NM expression, the following facts should be taken into account; Firstly, a given π-electron moves in the sea of electron clouds consisted of σ-electrons and other π-electrons, which forms a polarizable dielectric medium. According to the theory of dielectrics [*3*], the repulsion energy between two electrons in a dielectric is given by $E = e^2/(\varepsilon\, r_{12})$, where ε is the dielectric constant of the medium. r_{12} is the interelectron distance. For an interaction in micro dimension, ε should be replaced by the square of refractive index, n, of the medium. Consequently, $\gamma_{\mu\nu}$ should be given by

$$\gamma_{\mu\nu} = e^2/(n^{*2}\, r_{12})$$

where n^* means the effective refractive index which may vary with interatomic distance. Secondly, the electron correlation must be taken into account. Alternant molecular orbital method [*15*], split p-orbital method [*5*, *7*, *8*, *9*, *10*], and extraordinary function [*25*] were proposed for this purpose. They pointed out that the electrons in a π-system have a tendency to stay on opposite sides of the π-nodal plane. In benzene, six π-electrons are uniformally distributed. Probably, three of them are on the upper side of the molecular plane, and other three are lower side of this plane. Generally, in alternant hydrocarbons, π-electrons will be alternatively distributed to the "upper" and "lower" sides of the molecular plane. According to DEWAR-SABELLI [*10*], $\gamma_{\mu\nu}$ should be written by the form

$$\gamma_{\mu\nu} = C_1\, \gamma_{\mu\nu}^{uu} + C_2\, \gamma_{\mu\nu}^{ul}$$

where superscripts u and l denote upper and lower lobes of π-orbitals. Coefficients C_1 and C_2 are connected by $C_1 + C_2 = 1$ each other. Pariser-Parr replaced the normal integrals $\gamma_{\mu\nu}$ everywhere by the $\gamma_{\mu\nu}^{ul}$ corresponding to interactions between electrons on opposite sides of the nodal plane of the π-electron system [*10*]. However, it may be more reasonable to consider that γ_{12} and γ_{14} in benzene are the repulsion integrals between opposite sides electrons, whereas γ_{13} is associated with the same side electrons. Therefore, two types of the two center repulsion integrals should be defined. They are as follows;

$$\gamma_{\mu\nu}^{ul} = e^2/(n^{*2}\, r_{12}^{ul})$$
$$\gamma_{\mu\nu}^{uu} = e^2/(n^{*2}\, r_{12}^{uu})\,.$$

In this paper, interelectron distances are given by

$$r_{12}^{ul} = \sqrt{a_{\mu\nu}^2 + R_{\mu\nu}^2} \qquad \text{and} \qquad r_{12}^{uu} = (1/3)\left(\sqrt{a_{\mu\nu}^2 + R_{\mu\nu}^2} + 2\, R_{\mu\nu}\right)$$

where $a_{\mu\nu}$ is the characteristic constant for μ–ν pair and is expressed by the valence state ionization potential, I_μ, as $a_{\mu\nu} = (^1/_2)\ (a_\mu + a_\nu)$ and $a_\mu = e^2/I_\mu$. a_μ may probably measure the average distance between the center of μ-th core and an electron located at this core. Rough application of above expressions to the four lower transitions, three of them are singlets and another is the lowest triplet, of benzene shows that the valence state ionization potential of carbon $2p\pi$-orbital given by HINZE-JAFFÉ [13] is not appropriate, because when their value ($I_c = 11.16$ eV) is used, a strange result, $n^*\ (R = 2.790\ \text{Å}) < n^*\ (R = 1.395\ \text{Å})$ is obtained. The reason for this is probably they estimated the ionization potentials and electron affinities of the valence states of free atoms, but not of atoms in molecules. Proper value of $I_c\ (2p\pi)$ lies within the range between 8 eV and 10 eV. In this paper, I_c has been estimated by $I_c = I_{\rm H}\ r_{\rm H}/r_c$, where $I_{\rm H}$ and $r_{\rm H}$ are the ionization potential and van der Waals radii [22] of hydrogen atom, respectively. r_c is the halfthickness of aromatic hydrocarbons [22]. According to HINZE-JAFFÉ [13], the electron affinity of carbon $2p\pi$ AO is nearly zero. Therefore, γ_{11} is given by I_c in this case. Then, $\gamma_{11} = I_c = 9.60$ eV and $a_c = 1.50$ Å are obtained. n^{*2} is expressed by

$$n^{*2} = n_0^2\ (1 - 1/[k\ R_{\mu\nu} + n_0^2/(n_0^2 - 1)])\ .$$

n_0^2 and k are estimated from benzene spectrum as $k = 1.079/\text{Å}$ and $n_0^2 = 1.828$, or $n^{*2} = 1.828\ (R_{\mu\nu} + 1.127)/(R_{\mu\nu} + 2.060)$. It is interesting to note that the value of $n^*\ (R = \infty)$ which is equal to n_0 is comparable with the refractive indexes of aliphatic hydrocarbons.

Results and Discussions

SCF MO calculations of simple hydrocarbons based on the present idea, assuming equal bond distance of 1.395 A, have been carried out. For core integrals, the variable β approximation [19],

$$\beta_{\mu\nu} = -0.51\ P_{\mu\nu} - A_0\ \text{ eV}$$

where

$A_0 = 2.08$ for ethylene, butadienes, and benzene

$A_0 = 1.92$ for naphthalene ,

has been used, where $P_{\mu\nu}$ is the bond order for μ–ν pair. It is interesting to note that according to Pariser-Parr-Pople theory, the total π-energy of ethylene at the infinite separation is given by

$$E_\pi\ (R = \infty) = -\ 2\ I_c + (^1/_2)\ \gamma_{11} + 2\ \beta_{12}\ .$$

However, the value of $E_\pi\ (R = \infty)$ must be equal to $-\ 2\ I_c$. Using $\gamma_{11} = I_c = 9.60$ eV, β_{12} is determined as $\beta_{12} = -2.40$ eV, which is very close to the spectroscopic value of -2.59 eV. Therefore, the large part of $\beta_{\mu\nu}$ will be attributable to the correction term associated with the overestimation of ionic structure in LCAO MO approximation.

The calculated transition energies, first ionization potentials which are equal to the negative of the orbital energies of the highest occupied orbitals, and resonance energies are shown in Tab. 1. In Tab. 2, $\gamma_{\mu\nu}$'s are given.

It is found from Tab. 1 that the present idea gives satisfactory results for both singlet and triplet transition energies. Considerable improvement is found in the result for ^1L_a energy of naphthalene. Electronic spectra of cyclopentadiene will be very similar to those of cis-butadiene. Transition energies of cyclopentadiene are 5.21 eV [*23*] for lowest singlet and 2.5 eV [*11*] for lowest triplet, which are comparable with the present results.

Table 2. *Electron Repulsion Integrals, $\gamma_{\mu\nu}$, and Effective Refractive Index, n^**

$R_{\mu\nu}$ (in Å)	$\gamma_{\mu\nu}$ (in eV)	n^{*2}
0	9.60	1.0
1.395	5.260	1.335
2.416	3.885[a]	1.447
2.790	3.070	1.477
3.624	2.402	1.528
4.185	2.167[a]	1.555
4.832	1.855[a]	1.581
5.030	1.728	1.587

[a] upper-upper repulsion

It should be noted that the present parameters give good results for first ionization potentiasl of the hydrocarbons.

According to **Brickstock-Pople** [*4*], the resonance energy is given by the negative of the difference between the total π-energy of the actual system and the corresponding energy of the hypothetical system represented by one of its classical structures. The calculated resonance energies given in Tab. 1 are almost twice of the experimental values. In order to calculate accurate resonance energy, the compression energy and energies associated with the change in hybridizations should be known.

Acknowledgement. The author is pleased to thank Professor R. Fujishiro and Dr. K. Kimura for helpful discussion. It is also a pleasure to acknowledge valuable discussions with Professor N. Nakagawa of University of Electro-communications.

Table 1. *Transition Energies, First Ionisation Potentials, and Resonance Energies for Simple Hydrocarbons*

	Transition energy (in eV)										First ionization potential (in eV)		Resonance energy (kcal/mole)	
	Singlet								Lowest triplet					
	p-band		*α*-band		*β*-band		*β'*-band							
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
Ethylene	7.35	7.28 [*12*]							3.01	3.6 [*11*]	9.94	10.51 [*26*]	—	—
trans-Butadiene	5.49	5.71 [*14*]							2.44	2.6 [*11*]	8.78	9.07 [*26*]	14.9	3.5 [*1*]
cis-Butadiene	5.22	—							2.41	—	8.84	—	15.5	—
Benzene	6.23	6.20 [*6*]	4.88	4.88 [*6*]	6.94	6.93 [*6*]	6.94	6.93 [*6*]	3.71	3.64 [*17*]	9.49	9.245 [*26*]	74.7	41 [*1*]
Naphthalene	4.51	4.51 [*6*]	4.00	3.99 [*6*]	5.60	5.61 [*6*]	6.12	—	2.72	2.64 [*17*]	8.27	8.12 [*26*]	129.7	77 [*1*]

References

[*1*] Aston, J. G.: Determination of organic structures by physical methods, pp. 525 – 566. Ed.: Braude, E. A., and F. C. Nachod. New York: Academic Press 1955.
[*2*] Bloor, J. E., and F. Paradegordi: Theoret. chim. Acta [Berlin] **1**, 83 (1962).
[*3*] Bottcher, C. J. F.: Theory of electric polarization. New York: Elsevier 1952.
[*4*] Brickstock, A., and J. A. Pople: Trans. Faraday Soc. **50**, 901 (1954).
[*5*] Chung, A. L. H., and M. J. S. Dewar: J. chem. Physics **42**, 756 (1965).
[*6*] Clar, E.: Polycyclic hydrocarbons, Vol. **1**. New York: Academic Press 1964.
[*7*] Dewar, M. J. S., and C. F. Wulfman: J. chem. Physics **29**, 158 (1958).
[*8*] —, and N. L. Hojvat: J. chem. Physics **34**, 1232 (1961).
[*9*] — — Proc. Roy. Soc. [London] **A 264**, 431 (1961).
[*10*] —, and N. L. Sabelli: J. physic Chem. **66**, 2310 (1962).
[*11*] Evans, D. F.: J. chem. Soc. [London] **1960**, 1735.
[*12*] Hammond, V. J., and W. C. Price: Trans. Faraday Soc. **51**, 605 (1955).
[*13*] Hinze, J., and H. H. Jaffe: J. Amer. chem. Soc. **84**, 540 (1962).
[*14*] Kierstead, R. W., R. P. Linstead, and B. C. L. Weeden: J. chem. Soc. [London] **1953**, 1803.
[*15*] Løwdin, P. O.: Physic. Rev. **97**, 1509 (1955).
[*16*] —, and B. Pullman: Molecular orbitals in chemistry, physics, and biology. New York: Academic Press 1964.
[*17*] McClure, D. S.: J. chem. Physics **17**, 905 (1949).
[*18*] Nishimoto, K., and N. Mataga: Z. physik. Chem. [Frankfurt] **12**, 335 (1957).
[*19*] —, and L. S. Forster: Theoret. chim. Acta [Berlin] **3**, 407 (1965); **4**, 155 (1966).
[*20*] Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).
[*21*] Parr, R. G.: Quantum theory of molecular electronic structures. New York: W. A. Benjamin, Inc. 1963.
[*22*] Pauling, L.: The nature of the chemical bond, 3rd Ed. New York: Cornell University Press, Ithaca 1960.
[*23*] Peters, D.: J. chem. Soc. [London] **1959**, 1761.
[*24*] Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
[*25*] Snyder, L. C., and R. G. Parr: J. chem. Phys. **28**, 1250 (1958); **34**, 1661 (1961).
[*26*] Watanabe, K., T. Nakayama, and J. Mottl: J. Quant. Spectrosc. Radiat. Transfer **2**, 369 (1959).

Dr. Kichisuke Nishimoto
Department of Chemistry Faculty of Science
Osaka City University, Osaka (Japan)