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Some Remarks on the Pariser-Parr-Pople Method *

By

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Basic assumptions which characterize the PARISER-PARR-POPLE method of computing molecular electronic wave functions are critically examined. By restricted variational calculation of the valence state of carbon and nitrogen atoms and ions, it is demonstrated that the usual methods of evaluation of one-centre Coulomb integrals and atomic core energies are rather good. A semi-theoretical means of estimating the core resonance integral is proposed and shown to give fair agreement with the empirical values for C—C, O—O, C—N, and C—O bonds.

Die Grundannahmen der Methode von PARISER-PARR-POPLE zur Berechnung molekularer Wellenfunktionen werden kritisch durchleuchtet. Mittels beschränkter Variationsansätze für den Valenzzustand von Kohlenstoff- und Stickstoff-Atomen und -Ionen wird dargelegt, daß die Methoden, wie sie üblicherweise zur Berechnung von Einzentren-Coulombintegralen und atomaren Rumpfenergien angewendet werden, zu recht guten Ergebnissen führen. Ferner wird ein halbtheoretisches Verfahren zur Abschätzung der Rumpfresonanzintegrale vorgeschlagen und nachgewiesen, daß das Resultat gut mit den empirischen Werten für die C—C-, O—O-, C—N- und C—O-Bindung übereinstimmt.

Les hypothèses fondamentales de la méthode de PARISER-PARR-POPLE pour le calcul des fonctions d'onde électroniques sont examinées critiquement. Un calcul variationel limité des états de valence des atoms et ions de carbone et de nitrogène montre que les méthodes usuelles pour l'evaluation des intégrales de Coulomb monocentriques et des énergies de coeur atomiques sont assez bonnes. Nous proposons un procédé semithéorique pour évaluer l'intégrale de résonance de coeur, qui s'accorde assez bien aux valeurs expérimentales pour les liaisons C—C, O—O, C—N et C—O.

I. Introduction

In spite of the rapid progress in electronic computers in recent years, and its widespread influence on the computation of molecular wave functions, a need for a simple and effective semiempirical theory still exists, and will probably continue to exist for some time. The PARISER-PARR-POPLE method*** [*9*, *12*, *15*] is the most promising method to meet such a need for conjugated systems.

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*** This will be abbreviated to the P-P-P Method hereafter.

The method has been applied quite extensively to hydrocarbon molecules and also to a number of N- and O-containing heterocyclic molecules [*14*]. Good agreement with experiment has been obtained in these cases.

The P-P-P method involves a few basic assumptions which are foreign to the conventional method for calculating molecular electronic wave functions. There have been, therefore, several attempts to try to see the nature of these assumptions and to find out their functions and limitations. Particularly notable efforts have been made by PARR [*13*]. One aim of this paper is to reinforce this effort.

To treat the core resonance integrals as empirical parameters is one of the characteristic assumptions of the P-P-P method. This renders nice flexibility to the theory. However, if we want to apply the theory to big heterocyclic molecules, there appears quite a number of core resonance integrals, and it is difficult to treat all of them as empirical parameters. Another aim of this paper is to present a semi-theoretical means of evaluating core resonance integrals, though the estimate is bound to be very crude.

In the next section, a brief account of the P-P-P method is given. The nature of the assumption of the neglect of differential overlap and that of the so-called I-A correction is discussed in Section III and Section IV, respectively. In Section V, a semitheoretical estimate of core resonance integrals is described and discussed.

II. Characteristic Assumptions of the Pariser-Parr-Pople Method

The theoretical framework of the P-P-P method is the same as that of antisymmetrized product of molecular orbitals in the LCAO approximation with or without configuration interaction. It has been applied only to π-electron systems and the basic approximation is the σ-π separation. Thus the total wave function Φ is expressed as:

$$\Phi \sim \boldsymbol{A}\,[(\Sigma)\,(\Pi)]\ ,$$

where the antisymmetrized σ-part of the wave function (Σ) is assumed to be common to all the states in which we are interested. Under this approximation, it is possible to introduce an effective Hamiltonian $\boldsymbol{H}^{\pi}$ for the π-electron system:

$$\boldsymbol{H}^{\pi} = \sum_{i}^{(\pi)} \boldsymbol{f}(i) + \sum_{i<j}^{(\pi)} \frac{1}{r_{ij}}\ ,$$

where atomic units are used. The one-electron operator $\boldsymbol{f}$ consists of the kinetic energy operator and of the potential operator due to nuclei and σ-electrons. The total π-electron energy E^{π} can be written as:

$$E^{\pi} = \langle(\Pi)\,|\,\boldsymbol{H}^{\pi}\,|\,(\Pi)\rangle\ .$$

The P-P-P method differs from the orthodox method (sometimes called the ab-initio or non-empirical method) in the method of handling various molecular integrals. These molecular integrals are defined over basic atomic orbitals and appear in the energy expression E^{π}.

There are three basic assumptions in the P-P-P method:

(A) Neglect of differential overlap.

Whenever the expression $\chi_a(1)\,\chi_b(1)\,dv_1$ $(a \neq b)$ appears under an integral sign, the integral is put equal to zero, χ_a and χ_b are atomic orbitals centred on atom a and b respectively. This brings about enormous simplification. The overlap matrix becomes diagonal:

$$S_{ab} = \int \chi_a^* (1) \chi_b (1) \, dv_1 = \delta_{ab} ,$$

and the electron interaction integrals become

$$(ab \mid cd) \equiv \int \chi_a^* (1) \chi_b (1) \frac{1}{r_{12}} \chi_c^* (2) \chi_d (2) \, dv_1 \, dv_2 = \delta_{ab} \, \delta_{cd} \, (aa \mid cc) .$$

Thus all the difficult integrals – two-centre exchange and hybrid and many-centre integrals – disappear.

(B) The core resonance integrals between nearest neighbours are treated as empirical parameters. Those between non-neighbours are neglected.

(C) The one-centre Coulomb integrals $(aa \mid aa)$ are evaluated by the following formula:

$$(aa \mid aa) = I_a - A_a ,$$

where I_a and A_a are the ionization potential and the electron affinity of the orbital χ_a, when the atom a is in an appropriate valence state.

In order to carry out an actual calculation, we have to know how to evaluate the core Coulomb integrals and two-centre Coulomb integrals. Although the method of evaluation of these integrals is important for actual calculations, it is not as basic as the three assumptions mentioned above. We would not, therefore, go into details of the method in this paper.

III. The Zero Differential Overlap Approximation

The magnitude of overlap integrals between neighbouring $2p\pi$ orbitals in usual conjugated molecules is $0.25 \sim 0.33$. It looks, therefore, very drastic to neglect these quantities in comparison with 1.

Löwdin [6] and Parr [13] have suggested that this may be justified by assuming that the basic AO's used in the P-P-P method are Löwdin's symmetrically orthogonalized AO's ($\overline{\text{AO}}$'s) [5]. If orthogonalized AO's of this type are used as a basis, the overlap matrix is diagonal and many-centre integrals as well as two-centre hybrid and exchange integrals are generally very small in comparison with the two-centre Coulomb integrals [7]*.

A question arises in this connection: What is the repercussion of this interpretation on the values of other molecular integrals? The core resonance integrals and the one-centre Coulomb integrals are determined empirically so there is no problem about these**. The difference between two-centre Coulomb integrals defined over usual AO's and $\overline{\text{AO}}$'s are less than 0.23 eV for trans-butadiene,

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* The smallness of these integrals in the symmetrically orthogonalized AO basis is connected with the remarkable accuracy of the Mulliken approximation:

$$\chi_a (1) \chi_b (1) = \frac{S}{2} [\chi_a (1) \chi_a (1) + \chi_b (1) \chi_b (1)] ,$$

which is often used in evaluating many-centre integrals [2, 6].

** In fact, by using symmetrically orthogonalized AO's as the basis, it is possible to reproduce empirical values of the core resonance integrals by a semi-theoretical estimate (cf Section V).

cyclo-butadiene and benzene [*7*, *14*]. These differences can be shown to be small in general, by using again the Mulliken approximation [*2*], and can therefore be safely ignored.

The biggest difference occurs in the estimate of the core Coulomb integral. Let us discuss the homo-polar two-centre problem (e. g. C = C) for the sake of simplicity. Then the $\overline{\text{AO}}$ $\bar{\chi}_a$ can be expanded in terms of the original overlapping AO's χ_a and χ_b as follows:

$$\bar{\chi}_a = \left(1 + \frac{3}{8} S^2\right) \chi_a - \frac{1}{2} S \chi_b + O(S^3) \; . \tag{1}$$

Using this, we expand the core Coulomb integral $\bar{\alpha}^{\text{core}}$ and exchange integral $\bar{\beta}^{\text{core}}$

$$\bar{\alpha}^{\text{core}} \equiv (\bar{\chi}_a \,|\boldsymbol{f}|\, \bar{\chi}_a) = (1 + S^2)\, \alpha^{\text{core}} - S\, \beta^{\text{core}} + O(S^3) \; ,$$

$$\bar{\beta}^{\text{core}} \equiv (\bar{\chi}_a \,|\boldsymbol{f}|\, \bar{\chi}_b) = (1 + S^2)\, \beta^{\text{core}} - S\, \alpha^{\text{core}} + O(S^3) \; .$$

Eliminating β^{core} from these equations, we obtain

$$\bar{\alpha}^{\text{core}} = \alpha^{\text{core}} - S\, \bar{\beta}^{\text{core}} + O(S^3) \; .$$

The second term $-S\bar{\beta}^{\text{core}}$ is about 0.7 eV in C_2H_4 and C_6H_6. Although the change in α^{core}'s by changing the basis from AO's to $\overline{\text{AO}}$'s is not negligible, it seems certain that the changes are not excessive (less than 1 eV).

There is another set of orthogonalized AO's which might be considered as the basis in the P-P-P method. The whole space is split into regions and each AO has finite values within a particular region and vanishes identically outside of that region. The simplest way of making these orbitals is to cut off tails of each AO at the boundary of an allocated part and to renormalize it*.

The most attractive feature of these orbitals is that they satisfy rigorously the zero differential overlap condition. However, β^{core}'s are necessarily zero for these orbitals and this is clearly in contradiction to assigning non-zero values to these integrals. It should be remembered that the MO's are invariant by replacing AO's by $\overline{\text{AO}}$'s for the cases where the coefficients of AO's in these MO's are determined by the molecular symmetry (e. g. σMO in H_2, and πMO's in C_2H_4 and C_6H_6). If AO's are replaced by the cut-off AO's, the resulting MO's would not be able to describe the extra charge concentration between the nuclei when atoms are brought together. This charge concentration is necessary for binding. Thus there seems to be little hope in obtaining a satisfactory theory by using cut-off orbitals as the basis.

To conclude this section, we can perhaps say that by interpreting the basic AO's used in the PARISER-PARR-POPLE method as the symmetrically orthogonalized AO's, the zero-differential overlap assumption is justified (at least to some extent) and the other basic assumptions are unaffected.

IV. The I-A Correction

The procedure to evaluate the one-centre Coulomb integrals by the formula

$$(aa \mid aa) = I_a - A_a$$

is called the I-A correction.

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* The author's attention has been called to these orbitals independently by M. KOTANI, C. A. COULSON, and G. G. HALL.

This cannot be rationalized within the conventional MO LCAO scheme. The necessity of this correction is most easily understood by recalling Moffitt's observation [8] that the conventional MO LCAO method is bound to fail in predicting the energy difference between positive and negative ion pairs and two neutral atoms. This difference is experimentarily $I - A$. On the other hand, if we calculate the difference assuming the σ and π orbitals are the same in the ions and neutral atoms, we obtain simply the one-centre Coulomb integral $(aa \mid aa)$ for this energy difference. It is well known that calculated one-centre Coulomb integrals are much bigger than the I-A values.

The above argument is certainly crude. It has been pointed out by Brown and Heffernan that the form of the AO's should depend on the electron density at that atom [1]. It seems worth-while to examine the situation more carefully by directing our attention to the dependence of the π and σ-core functions on the π charge density.

Let us take the carbon atom as an example. The energies of a positive ion E [C^+], of a negative ion E [C^-] and of a neutral atom E [C] are then expressed as follows:

$$\begin{aligned} E\,[C^+] &= E^+(\sigma), \\ E\,[C^-] &= E^-(\sigma) + 2\,W\,(1.2) + (aa \mid aa), \\ E\,[C] &= E\,(\sigma) + W\,(1.1), \end{aligned}$$

where $W\,(n, q)$ is defined by

$$W\,(n, q) = \left(\chi\,(q) \mid -\frac{1}{2}\Delta + \boldsymbol{v}\,(n, q) \mid \chi\,(q)\right) .$$

Here, $\boldsymbol{v}$ is the potential due to the σ-core, n is the number of π-electron contributed to the π-electron system from the atom (e. g. for C and pyridine-type N, $n = 1$; and for pyrrole-type N, $n = 2$) and q is the π-electron charge density on the atom ($q = 1$ for C, 2 for C^-). The potential $\boldsymbol{v}$ depends not only on n which determines the number of σ-electrons but also on q, because the σ-core is deformed due to the π-charge density.

If the q dependence of the quantity W is small, namely $W\,(1.2) \div W\,(1.1)$, we then obtain

$$I - A = (aa \mid aa) + [E^+(\sigma) + E^-(\sigma) - 2\,E\,(\sigma)] .$$

The second term on the right-hand side always accompanies $(aa \mid aa)$ and we can regard the I-A value as representing the whole righthand side. Therefore, we may set aside the second term for the moment.

The crucial and interesting question seems to be whether $W\,(n, q)$ is really insensitive to q or not. To answer this question is difficult. In order to get an estimate, we have calculated this quantity for C and N in their valence states, using Slater-type AO's. In the calculation, orbital exponents of $1\,s$, $2\,s$, $2\,p\,\sigma$ and $2\,p\,\pi$ orbitals are varied freely so as to make the energy minimum.

The results of the calculations are shown in Tab. 1, 2 and 3.

From these tables, it is seen that, in spite of the noticeable changes in both σ and π orbitals, $W\,(n, q)$ is fairly insensitive to the q value for C and pyrrole-type N. The difference is as much as -1.8 eV for pyridine-type N but we should

Table 1. *Valence state energy of* C *(in eV)*

	C^+	C	C^-
Electron configuration	$(sp^2)^3$	$(sp^2)^3\pi$	$(sp^2)^3\pi^2$
Orbital exponent of 1*s*	5.65	5.65	5.65
Orbital exponent of 2*s*	1.76	1.65	1.58
Orbital exponent of 2 *pσ*	1.82	1.64	1.53
Orbital exponent of 2 *pπ*	—	1.63	1.30
Total energy	—1012.64	—1022.53	—1018.43
σ-core energy	—1012.64	—1011.60	—1009.90
W	—	—10.94	—11.24
$(\pi\pi \mid \pi\pi)$	—	17.36	13.95

Table 2. *Valence state energy of pyridine-type* N *(in eV)*

	N^+	N	N^-
Electron configuration	$(sp^2)^4$	$(sp^2)^4\pi$	$(sp^2)^4\pi^2$
Orbital exponent of 1*s*	6.65	6.64	6.64
Orbital exponent of 2 *s*	2.04	1.94	1.86
Orbital exponent of 2 *p σ*	2.15	1.96	1.79
Orbital exponent of 2 *p π*	—	1.98	1.72
Total energy	—1461.96	—1474.27	—1469.59
σ-core energy	—1461.96	—1458.76	—1460.43
W	—	—15.51	—13.74
$(\pi\pi \mid \pi\pi)$	—	21.09	18.32

Table 3. *Valence state energy of pyrrole-type* N *(in eV)*

	N^{++}	N^+	N
Electron configuration	$(sp^2)^3$	$(sp^2)^3\pi$	$(sp^2)^3\pi^2$
Orbital exponent of 1*s*	6.65	6.64	6.64
Orbital exponent of 2 *s*	2.19	2.08	1.98
Orbital exponent of 2 *p σ*	2.33	2.15	1.99
Orbital exponent od 2 *p π*	—	2.16	1.91
Total energy	—1434.27	—1462.74	—1471.56
σ-core energy	—1434.27	—1433.19	—1430.45
W	—	—29.55	—30.72
$(\pi\pi \mid \pi\pi)$	—	23.00	20.34

remember that in actual molecules, the N atom never has a π-electron charge as great as 2, and the above difference may be regarded as an upper bound.

A usual procedure to evaluate $W\ (n, q)$ is to use the following relation:

$$W\ (n, q) = -I_n\ ,$$

where I_n is the *n*th valence state ionization potential. The values of I_n are 11.16, 14 12, and 28.71 eV respectively [4]. We see, therefore, the usual estimate involves errors of less than 1 eV for C and N.

The conclusions from the present calculations are (a) that effects due to changes of orbitals tend to cancel each other and the net changes are rather small and (b) that the usual assumption

$$W\ (n, 1) = W\ (n, 2) = -I_n$$

is valid within an error of 1 eV. It should be emphasized that these conclusions are reached on the basis of calculations which are more general than the simple minded method of using the same AO's for positive and negative ions as well as neutral atoms, but are still very limited. The present calculation is especially inadequate for negative ions. Calculated electron affinities are negative and as large as 4 ~ 5 eV. A single Slater AO is not adequate for describing the long tail of the charge cloud of a negative ion. In order to obtain a decent electron affinity value, we probably have to use two or more terms with different orbital exponents for the orbital of a negative ion.

V. Semi-Theoretical Estimate of Core Resonance Integrals

The aim of this section is to propose a crude semi-theoretical expression of core resonance integrals by which we can estimate their values in case it is difficult to determine them semiempirically by some reason (e. g. due to lack of experimental data or simply because there are too many β's).

Let us assume that the basic AO's in the P-P-P method are Löwdin-type symmetrically orthogonalized AO's. We simplify the problem to that of two centres and neglect the presence of other atoms. Using the expansion (1), we obtain:

$$\bar{\beta}_{ab}^{\mathrm{core}} = \beta_{ab}^{\mathrm{core}} - \frac{1}{2} S\,(\alpha_a^{\mathrm{core}} + \alpha_b^{\mathrm{core}}) + O\,(S^2) \ .$$

The operator $\boldsymbol{f}$ may be assumed to have the following form:

$$\boldsymbol{f} = -\frac{1}{2}\Delta + \boldsymbol{v}_a + \boldsymbol{v}_b \ ,$$

where $\boldsymbol{v}_a$ is the potential due to the σ-core of atom a. Next we introduce the Mayer-Sklar approximation [3]*:

$$\left(\chi_b \,\middle|\, -\frac{1}{2}\Delta + \boldsymbol{v}_a \,\middle|\, \chi_a\right) = S\left(\chi_a \,\middle|\, -\frac{1}{2}\Delta + \boldsymbol{v}_a \,\middle|\, \chi_a\right) \ . \tag{2}$$

Neglecting the second and higher terms of S, we then obtain

$$\bar{\beta}_{ab}^{\mathrm{core}} = \frac{1}{2}\,[(a\,|\,\boldsymbol{v}_a\,|\,b) + (b\,|\boldsymbol{v}_b\,|\,a)] - \frac{1}{2} S\,[(a\,|\,\boldsymbol{v}_b\,|a) + (b\,|\,\boldsymbol{v}_a\,|\,b)] \ .$$

In the homopolar case, the equation reduces to

$$\bar{\beta}_{ab}^{\mathrm{core}} = (a\,|\,\boldsymbol{v}_a\,|\,b) - S\,(a\,|\,\boldsymbol{v}_b\,|\,a) \ . \tag{3}$$

The integral $(a \,|\, \boldsymbol{v}_b \,|\, a)$ may be approximated as follows

$$(a\,|\,\boldsymbol{v}_b\,|\,a) \sim n\,(aa\,|\,bb) \ . \tag{4}$$

The integral $(a \,|\, \boldsymbol{v}_a \,|\, b)$ is more difficult to evaluate. The significant part of this integral would come from the region near the mid-point of the internuclear separation. The value of the potential at the mid-point is $-\frac{n}{R/2}$. We replace the potential by this constant value and integrate; the result is

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* The Mayer-Sklar approximation in its original form is

$$\left(-\frac{1}{2}\Delta + \boldsymbol{v}_a\right)\chi_a = W_a\,\chi_a \ .$$

Eq. (2) can be derived from the above relation but has probably a wider range of applicability.

$$(a \,|\, \boldsymbol{v}_a \,|\, b) \sim -\, n S \frac{2}{R} \ . \tag{5}$$

Substituting (4) and (5) in (3), we arrive at

$$\overline{\beta}^{\,\mathrm{core}}_{ab} = n S \left[-\frac{2}{R} + (aa \,|\, bb) \right] \ . \tag{6}$$

There is no doubt that this estimate is very crude. We have neglected the effects of atoms other than a and b and higher order terms of S and have used approximations (2), (4), and (5). However the weakest link is probably the approximation (5). We would like to introduce a constant factor C on the right-hand side of Eq. (5) and by this modification we obtain the final expression:

$$\overline{\beta}^{\,\mathrm{core}}_{ab} = n S \left[-\frac{2C}{R} + (aa \,|\, bb) \right] \ . \tag{7}$$

The extension to heteropolar two-centre cases under the same approximations is straightforward. The values calculated by Eq. (7) are compared with empirically-determined β values in Tab. 4.

Table 4. *Values of Core Resonance Integral (in eV)*

Molecule	R (Å)	Empirical	Calculated		
			Eq (3)	*Eq* (7)[4] (C = 1)	*Eq*(7)[4] (C = 0.85)
C_2H_4	1.35	—2.92[1]	—2.80	—3.80	—2.91
C_6H_6	1.39	—2.39[1]	—2.63	—3.42	—2.61
O_2	1.16	—5.38[2]	—4.16	—7.46	—5.63
O_2	1.28	—3.28[2]	—2.98	—4.96	—3.73
O_2	1.40	—2.39[2]	—	—3.25	—2.43
O_2	1.51	—1.96[2]	—	—2.13	—1.58
O_2	1.63	—1.69[2]	—	—1.40	—1.04
CN	1.36	—2.58[1]	—	—2.75	—2.09
CO	1.22	—2.86[3]	—	—3.18	—2.42

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[1] PARISER, R., and R. G. PARR: J. chem. Physics **21**, 767 (1953).

[2] FUMI, F. G., and R. G. PARR: J. chem. Physics **21**, 1864 (1953).

[3] OHNO, K: Unpublished result.

[4] Overlap integrals are calculated by using Slater's orbitals. Two-centre Coulomb integrals are evaluated by the formula

$$(aa \,|\, bb) = \frac{1}{\sqrt{R^2 + d^2}} \, , \quad \frac{1}{d} = I - A \ .$$

In Tab. 4, values of the right-hand side of Eq. (3) obtained by using the purely theoretical molecular integrals [*10, 11*] are listed in Column 4. These values are not so different from the empirical values. This indirectly supports the analysis leading to Eq. (3). In the case of C_6H_6, we can also estimate the effect of potential due to the presence of atoms other than a and b. These potentials being included, the calculated value becomes -3.19 eV.

In Column 6, the value of $C = 0.85$ was chosen just because it seems to give a fair overall fit to the empirical values in the chosen cases. The agreement between the values in Column 3 and 7 is certainly not as good as we hope to obtain. Nevertheless, the author feels that the proposed formula (7) may be useful in getting the first approximation.

Summary

One of the characteristic assumptions of the P-P-P method, namely the I-A correction, was critically examined by taking into account deformation of both σ-core and π-orbitals due to different π charge densities. Variational calculation of valence state energies of carbon and nitrogen atoms and ions were carried out by assuming Slater-type AO's but by varying their orbital exponents. The results of the calculations indicate that the effect of this deformation on the I-A correction is not very large. The results also indicate that the usual estimate of atomic core energy (denoted in this article by W) as $-I$ is valid to within about 1 eV.

Some arguments are presented for the interpretation that the basic AO's in the P-P-P method are the Löwdin-type orthogonalized AO's. On the basis of this interpretation, a crude but simple expression for the core resonance integral was proposed. The estimate by this expression gives fair agreement with the empirical values for C—C, O—O, C—N, and C—O bonds.

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