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Convenient Quadratic Formulas for the Two-center Coulomb Repulsion Integrals in the Semiempirical LCAO-MO Method and the Significance of the Pariser-Parr Approximation[1]

Yasuhiko GONDO and Yoshiya KANDA
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka

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The coefficients in the Pariser-Parr-type quadratic formulas for the two-center Coulomb repulsion integrals encountered in the planar as well as the non-planar conjugated systems have been expressed as linear functions of the effective nuclear charges of the $2p$ atomic orbitals involved. The formulas thus obtained are applicable to those conjugated systems consisting of carbon, nitrogen, and oxygen atoms, and may well be useful in variable-electronegativity self-consistent field calculations on these systems. With some illustrative applications to spin densities and phosphorescent-state energies, it has been shown that the Pariser-Parr approximation gives better results than the Nishimoto-Mataga one, although the latter is successful in the prediction of electronic transitions within the singlet manifold. Incidentally, this was also the case for the phosphorescent-state zero-field splittings (Y. Gondo and Y. Kanda, This Bulletin, **43**, 3943 (1970)). The electric dipole moments have also been discussed.

As is well known, in the Pariser-Parr-Pople method[2,3] the two-center Coulomb repulsion integrals are evaluated semiempirically for smaller interatomic distances, and several kinds of approximations have been proposed for this purpose.[4,5] Among them, the Nishimoto-Mataga approximation[6] is distinctly different from the others in giving nearest-neighbor values smaller than those of the others by nearly 2 eV.[5] As for the others, they are practically identical with each other; the Pariser-Parr approximation may be regarded as a prototype. The Nishimoto-Mataga approximation has been employed quite extensively and frequently because of its simplicity, its successful prediction of electronic transitions within the singlet manifold, and also its easy adaptability to variable-electronegativity self-consistent field (VESCF) calculations.[7,8]

However, in the prediction of triplet-state zero-field splittings (ZFS), for example, a Pariser-Parr-type (PP-type) quadratic formula is much better than a Nishimoto-Mataga-type (NM-type) one, as has previously been pointed out by the present authors.[9] In addition, a PP-type formula gives better results with regard to the phosphorescent-triplet-state energies of neutral molecules and the spin densities in the molecular ions than does a NM-type formula, as will be described later. The electric dipole moments of neutral molecules will also be discussed.

Thus, if we have a PP-type formula as simple as a NM-type formula, it can be invoked as extensively and frequently as the latter. In this paper, it will be shown that the coefficients appearing in the PP approximation are linearly dependent on the effective nuclear charges of the AO's involved, subject to the Paoloni-type approximations[10] for the one-center Coulomb repulsion integrals. All the two-center Coulomb repulsion integrals encountered in the planar as well as the non-planar conjugated systems consisting of carbon, nitrogen, and oxygen atoms have been studied jointly. The formulas thus obtained are easily adaptable to the VESCF calculations of these systems.

Incidentally, the very difference of 2 eV for the nearest neighbors is significant, as is suggested by the clearly different results on the various molecular properties mentioned above. Since this may be closely associated with the problem of electronic correlation in molecules,[11,12] it is desirable to accumulate as many results as possible with the PP approximation as well in

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[1] Presented in part at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[2] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[3] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[4] K. Ohno, "Advances in Quantum Chemistry," Vol. 3, ed. by P. O. Löwdin, Academic Press, New York 1967, p. 239.

[5] T. Anno, "Bunshi Kagaku Koza," Vol. 3, ed. by T. Nakajima, Kyoritsu, Tokyo 1966, p. 232.

[6] K. Nishimoto and N. Mataga, *Z. Phys. Chem.* (Frankfurt), **12**, 335 (1957).

[7] P. J. Black and C. A. McDowell, *Mol. Phys.*, **12**, 233 (1967).

[8] R. D. Brown and B. A. W. Coller, *Theor. Chim. Acta*, **7**, 259 (1967).

[9] Y. Gondo and Y. Kanda, This Bulletin, **43**, 3943 (1970).

[10] L. Paoloni, *Nuovo Cimento*, **4**, 410 (1956).

[11] P. O. Löwdin, "Advances in Chemical Physics," Vol. II, ed. by I. Prigogine, Interscience Publishers, New York 1959, p. 207.

[12] *Ibid.*, Vol. XIV, ed. by R. Lefebvre and C. Moser (1969).

order to gain a better understanding of this interesting but intractable problem. In this context, the convenient formulas we have obtained might be of some use.

General Remarks

The symbols σ, π, and $\bar{\pi}$ stand for $2p\sigma$, $2p\pi$, and $2p\bar{\pi}$ respectively.[13] In the planar conjugated systems, every two-center Coulomb repulsion integral $(pp|qq)$ is of the $(\pi_p\pi_p|\pi_q\pi_q)$ type, whereas this is not the case for the non-planar systems. Thus, we have the following expression, in general:[14]

$$\begin{aligned}(pp|qq) = {} & \omega_1(\sigma_p\sigma_p|\sigma_q\sigma_q) + \omega_2(\sigma_p\sigma_p|\pi_q\pi_q) \\ & + \omega_3(\pi_p\pi_p|\sigma_q\sigma_q) + \omega_4(\pi_p\pi_p|\pi_q\pi_q) \\ & + \omega_5(\pi_p\pi_p|\bar{\pi}_q\bar{\pi}_q) + \omega_6(\pi_p\bar{\pi}_p|\pi_q\bar{\pi}_q) \\ & + \omega_7(\sigma_p\pi_p|\sigma_q\pi_q),\end{aligned} \tag{1}$$

where the coefficients ω_1, ω_2,$\cdots$are determined by the relative orientation of the $2p$ AO's involved.

According to Pariser and Parr,[2] for interatomic distances smaller than 2.8 Å each of the basic integrals in Eq. (1) may be evaluated by means of the quadratic extrapolation formula:

$$(\mu_p\mu_p'|\nu_q\nu_q') = C_0 + C_1R + C_2R^2, \tag{2}$$

where μ, μ', ν, and ν' stand for σ, π, or $\bar{\pi}$, and where R is the pertinent interatomic distance. In addition, C_0 is defined by the relation:

$$C_0 = [(\mu_p\mu_p'|\nu_p\nu_p') + (\mu_q\mu_q'|\nu_q\nu_q')]/2. \tag{3}$$

The one-center integrals in Eq. (3) can be obtained through the expressions listed under "Semiempirical" heading in Table 1; these expressions have been derived on an assumption of the same proportionality between the theoretical and the semiempirical values for every type of basic integral[15] as that for $(\pi\pi|\pi\pi)$, which is in turn based on Paoloni's relation.[10] These theoretical one-center integrals have been obtained with the Slater-type AO's and the formulas of Roothaan.[13] The effective nuclear charges used are 3.25, 3.90, and 4.55 for carbon, nitrogen, and oxygen respectively.

Table 1. One-center coulomb repulsion integrals involving $2p$ atomic orbitals[a)]

Integral	Theoretical[b)]	Semiempirical
$(\sigma\sigma\|\sigma\sigma)=(\pi\pi\|\pi\pi)$	5.325 Z	3.294 Z[c)]
$(\sigma\sigma\|\pi\pi)=(\pi\pi\|\bar{\pi}\bar{\pi})$	4.751 Z	2.939 Z
$(\sigma\pi\|\sigma\pi)=(\pi\bar{\pi}\|\pi\bar{\pi})$	0.2870 Z	0.1775 Z

a) Z stands for the effective nuclear charge.
b) Obtained with the Slater-type AO's and the formulas given by Roothaan.[13]
c) Paoloni's relation.[10]

For interatomic distances larger than 2.8 Å, the multipole expansion formula can be used without decomposing $(pp|qq)$ into the basic integrals.[16] It should be noted that the multipole expansion formula has a simple dependence on the effective nuclear charges of the AO's involved; hence, it is easily adaptable to the VESCF calculation.

The C_1 and C_2 Coefficients

The Use of Multipole Expansion Formulas for Obtaining the C_1 *and* C_2 *Coefficients.* The coefficients, C_1 and C_2, of Eq. (2) for every basic integral in Eq. (1) have been determined originally with the C_0 of Eq. (3) and with the corresponding two-center integrals, obtained at 2.8 and 3.7 Å with the multipole expansion formulas.[16] The largest deviation of the integrals obtained with these formulas from those obtained with the theoretical formulas of Roothaan[13] has been found for the basic integral $(\sigma\sigma|\sigma\sigma)$; it is, at most, for example, 1% for the C–C pair at 2.75 Å. For the second to fifth basic integrals in Eq. (1), however, the deviations are of the order of 0.01% at the same distance. As for the rest, they are intrinsically very small quantities, and practically no deviations are found down to three decimal places in electron-volts at the same distance as above. In addition, the coefficient multiplying $(\sigma\sigma|\sigma\sigma)$ in Eq. (1) is usually small. Therefore, the use of the multipole expansion formulas may be justified.

Linear Dependence of C_1 *and* C_2 *on the Effective Nuclear Charges.* The coefficients, C_1 and C_2, thus obtained have been found expressible as linear functions of the effective nuclear charges of the AO's involved, as is shown in Fig. 1, for example, for the basic integral $(\pi\pi|\pi\pi)$. The linear functions have been obtained through the method of least-squares; they are collected in Table 2. These results reproduce the integral values obtained with the original coefficients, C_1 and C_2, for example, at 1.5 Å within a margin of 0.3% for the first, 0.1% for the second to fifth, 0.4% for the sixth, and 1% for the last basic integral of Eq. (1). As has been mentioned above, in Eq. (1) the coefficient, ω_1, is usually small, and the last two basic integrals are of intrinsically very small quantity. Therefore, it may be concluded that the results collected in Table

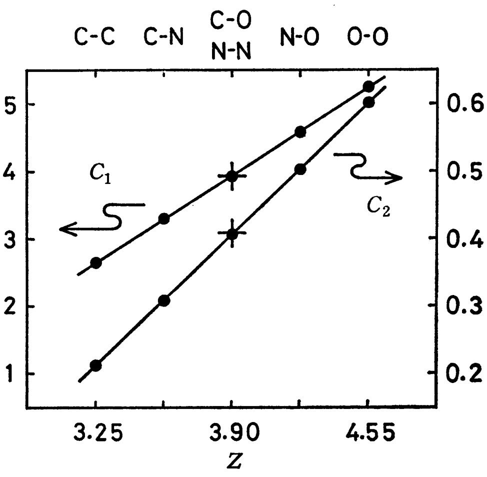

Fig. 1. Linear depencence of the C_1 and C_2 coefficients on the arithmetic mean of the effective nuclear charges of the AO's involved, Z, in the basic integral $(\pi\pi|\pi\pi)$. With Z=3.90, the crosses refer to the C–O pair.

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13) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).
14) Y. Gondo, *ibid.*, **41**, 3928 (1964).
15) R. Hoffmann, A. Imamura, and G. Zeiss, *J. Amer. Chem. Soc.*, **89**, 5215 (1967).
16) R. G. Parr, *J. Chem. Phys.*, **33**, 375 (1960).

TABLE 2. THE COEFFICIENTS IN THE QUADRATIC FORMULAS FOR THE TWO-CENTER COULOMB REPULSION INTEGRALS[a)]

Integral	C_0	C_1	C_2
$(\sigma\sigma \mid \sigma\sigma)$	$3.294\,Z$	$5.5778-2.2985\,Z$	$-1.1900+0.3748\,Z$
$(\sigma\sigma \mid \pi\pi)$	$2.939\,Z$	$4.4455-0.9999\,Z\sigma-0.8697\,Z\pi$	$-0.9112+0.1605\,Z\sigma+0.1291\,Z\pi$
$(\pi\pi \mid \pi\pi)$	$3.294\,Z$	$3.8360-1.9934\,Z$	$-0.7661+0.3004\,Z$
$(\pi\pi \mid \bar{\pi}\bar{\pi})$	$2.939\,Z$	$3.7923-1.7617\,Z$	$-0.7549+0.2639\,Z$
$(\pi\bar{\pi} \mid \pi\bar{\pi})$	$0.1775\,Z$	$0.0219-0.1158\,Z$	$-0.0056+0.0183\,Z$
$(\sigma\pi \mid \sigma\pi)$	$0.1775\,Z$	$0.0875-0.1293\,Z$	$-0.0224+0.0217\,Z$

a) Z stands for the arithmetic mean of the effective nuclear charges of the AO's involved. Lengths are given in angstroms, and energies, in electron-volts in Eq. (2).

2 reproduce the integral values calculated with the original coefficients within a margin of 0.1%.

Further Remarks on $(\pi\bar{\pi}|\pi\bar{\pi})$ *and* $(\sigma\pi|\sigma\pi)$. From the symmetry and R-dependence, the basic integrals, $(\pi\bar{\pi}|\pi\bar{\pi})$ and $(\sigma\pi|\sigma\pi)$, are distinguished from the rest. Since these integrals are themselves intrinsically very small, the relevant quadratic formulas sometimes give negative values, even for interatomic distances smaller than 3.0 Å, although they must be positive in principle. Further, the integral values are smaller than 0.02 eV at 3.0 Å. Therefore, it may be concluded that these basic integrals can be neglected if the interatomic distance is larger than 3.0 Å or if the calculated integral values are found to be negative.

Some Illustrative Applications

In this concluding section, as was mentioned in the introduction, some examples will be presented in order to illustrate the usefulness of the PP approximation through the use of the convenient formulas obtained in the preceding section, although these examples are chosen rather arbitrarily and are restricted to the planar conjugated systems. In what follows, the wavefunctions are calculated by means of a method described previously,[9,17)] and by means of the effective nuclear charges of 3.25 and 3.90 for carbon and nitrogen respectively in the usual SCF scheme. In the VESCF calculations, the dependences of the effective nuclear charges and valence-state ionization potentials on the charge densities are incorporated by the use of the procedure adopted by Brown and Heffernan;[18)] moreover, all the parameters are variable, unless otherwise specified.

The Energies of the Phosphorescent Triplet States. The excitation energies of the phosphorescent triplet states of some aromatic hydrocarbons and nitrogen heterocycles are predicted by the PP approximation much better than by the NM approximation, as is shown in Table 3. Tyutyulkov, Gochev, and Fratev[19)] also noted this, and modified a NM formula in order to remedy this shortcoming. They stated that their formula was as simple as the original one and that it was successful in the prediction of singlet-singlet transitions. However, it hardly seems acceptable, not only in the sense that it has no correct asymptotic behavior for sufficiently large distances, such behavior as the original formula shows, but also in the sense that it gives significant deviations from the theoretical values at intermediate distances larger than 2.8 Å.

TABLE 3. THE EXCITATION ENERGIES OF THE PHOSPHORESCENT TRIPLET STATES (eV)

Compound[a)]	Calculated Approximation for $(pp \mid qq)$[b)] NM	 PP	Obsd
Benzene	2.64	3.56	3.66[c)]
Naphthalene	1.82	2.53	2.64[c)]
Quinoline	1.73	2.49	2.69[c)]
Isoquinoline	1.77	2.50	2.63[d)]
Quinoxaline	1.54	2.31	2.65[c)]
Anthracene	1.09	1.67	1.85[c)]
Phenanthrene	1.85	2.56	2.69[e)]
1,10-Phenanthroline	1.78	2.55	2.74[f)]
5,6-Benzoquinoline	1.80	2.54	2.71[e)]
7,8-Benzoquinoline	1.81	2.56	2.70[e)]
Triphenylene	2.10	2.88	2.95[g)]

a) For the structural formulas, see Ref. 9.
b) For the abbreviations, see the text.
c) to g) Ref. 20 to 24 respectively.

Since the development of this kind of modification may be due to the need for a foumula as simple and useful as the NM one, the formulas proposed in this paper seem to acquire justification. In particular, any conjugated systems consisting of carbon, nitrogen, and oxygen atoms are within the scope of these formulas. Moreover, these are easily adaptable to the VESCF procedure, which has been demonstrated to be useful for the prediction of the electric dipole moments of various organic compounds.[8)]

Incidentally, it should be noted that the approximation that gives better results on the state energies also leads to better results on the ZFS parameters.[9)]

The Electric Dipole Moment of the Ground State of Azulene

[17)] Y. Gondo and A. H. Maki, *J. Chem. Phys.*, **50**, 3270 (1969).

[18)] R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

[19)] N. Tyutyulkov, A. Gochev, and F. Fratev, *Chem. Phys. Lett.*, **4**, 9 (1969).

[20)] S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State," Prentice-Hall, Englewood Cliffs, New Jersey (1969), Chap. 4.

[21)] F. Dörr and H. Gropper, *Ber. Bunsenges. Phys. Chem.*, **67**, 193 (1963).

[22)] Y. Kanda and R. Shimada, *Spectrochim. Acta*, **15**, 211 (1959).

[23)] H. Gropper and F. Dörr, *Ber. Bunsenges. Phys. Chem.*, **67**, 46 (1963).

[24)] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

and the Spin Densities in Its Anion. Azulene is chosen for two reasons—first, because it is a non-alternant hydrocarbon, and second, because the complex problem of a correct allowance of the electronic effects of heteroatoms does not, of course, arise.[8] The first reason is based on the observation of Ruedenberg[25] that the results of calculations on the polycyclic alternant hydrocarbons are more strongly dependent on their topological matrix than on the choice of repulsion or resonance integrals.

TABLE 4. CALCULATED ELECTRIC DIPOLE MOMENTS OF THE GROUND STATE OF AZULENE[a] (D)

Method[b]	Approximation for $(pp\,|\,qq)$[c]	
	NM	PP
S1	2.735	2.464
S2	2.170	2.039
V1	2.196	2.066
V2	1.698	1.648
W1	2.140	2.021
W2	1.652	1.608
Observed[d]	0.796±0.014	

a) For the defined positive direction of the dipole moment, see Fig. 2.
b) S: SCF; V: VESCF; W: VESCF, except for $(pp|qq)$, for which the neutral-atom effective nuclear charges are used; 1 and 2: Core resonance integrals are taken into account up to nearest neighbors and next-nearest neighbors respectively.
c) For the abbreviations, see the text.
d) Ref. 26.

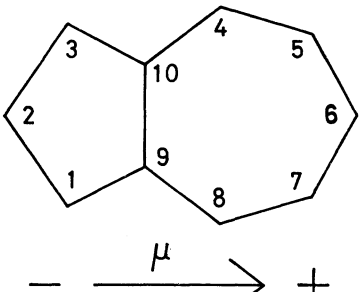

Fig. 2. The carbon skeleton of azulene and the defined positive direction of the electric dipole moment, μ, with the numbering of atoms.

The electric dipole moments obtained for the ground state by various methods are collected in Table 4, in which the contributions from the σ-electrons are not taken into account.[8] The molecular geometry adopted is based on the x-ray data after averaging according to the molecular symmetry.[27] As this table shows, the VESCF procedure and the inclusion of the next-nearest-neighbor resonance integrals[28] improve the results considerably.

TABLE 5. CALCULATED π-ELECTRONIC CHARGE DENSITIES IN THE GROUND STATE OF AZULENE[a]

Atomic position	Approximation for $(pp\,|\,qq)$[b]	
	NM	PP
1,3	1.0643	1.0706
2	0.9993	0.9904
4,8	0.9575	0.9513
5,7	1.0019	1.0071
6	0.9682	0.9671
9,10	0.9926	0.9923

a) Obtained by means of the V2 method, as defined in Table 4.
b) For the abbreviations, see the text.

Brown and Coller[8] have stated that the PP approximation has a tendency to give larger π-moments than the NM. However, this does not seem to be confirmed even by their own results. The present results on azulene also contradict this statement. The most characteristic difference between the NM and PP approximations seems to be that the latter gives larger absolute values to the net charge densities than the former; that is, the alternation in the charge distribution derived through the latter is more distinct than that due to the former, as can be seen, for example, from the entries of Table 5. This is also found for furan, pyrrole, and pyridine.[8] In the VESCF procedure, this characteristic difference seems to be blurred to an appreciable extent, but it still survives, as may be seen in Table 5. Brown and Coller[8] did not incorporate the dependence of $(pp|qq)$ integrals on the effective nuclear charges in their VESCF scheme; their scheme is obviously an improvement, as is revealed by a comparison of the relevant entries in Table 4.

TABLE 6. CALCULATED SPIN DENSITIES AND EXPECTATION VALUES OF $\mathbf{S}^2$ FOR AZULENE ANION AFTER SINGLE ANNIHILATION[a]

Atomic position	Approximation for $(pp\,|\,qq)$[b]		a^{H}[c] (Gauss)
	NM	PP	
1,3	0.108	−0.020	0.274
2	0.055	0.140	3.948
4,8	0.375	0.223	6.219
5,7	−0.283	−0.083	1.338
6	0.442	0.359	8.829
9,10	0.051	0.131	
$<\mathbf{S}^2>$	0.694	0.748	

a) Based on the single-determinant UHF wavefunctions obtained with the V2 method, as defined in Table 4, and the same molecular geometry as was used for the neutral molecule. For the annihilation procedure, see Ref. 29.
b) For the abbreviations, see the text.
c) Absolute values of the experimental splitting constants. See Ref. 30.

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25) K. Ruedenberg, *J. Chem. Phys.*, **34**, 1861 (1961).
26) H. J. Tobler, A. Bauder, and H. H. Günthard, *J. Mol. Spectrosc.*, **18**, 239 (1965).
27) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Crystallogr.*, **15**, 1 (1962).
28) R. D. Brown, F. R. Burden, and G. M. Mohay, *Aust. J. Chem.*, **21**, 1695 (1968).
29) T. Amos and L. C. Snyder, *J. Chem. Phys.*, **41**, 1773 (1964).
30) I. Bernal, P. H. Rieger, and G. K. Fraenkel, *ibid.*, **37**, 1489 (1962).

The spin densities and the expectation values of $\mathbf{S}^2$ in the azulene anion are predicted by the PP approximation much better than by the NM, as Table 6 shows. This has also been confirmed with various aromatic nitrogen heterocycles.[7,31] By multiplying these spin densities by the $Q^{\mathrm{H}}_{\mathrm{CH}}$ value of -23G for a CH bond in an aromatic system,[30] those from the PP approximation are found to reproduce the experimental splitting constants very well, whereas with those of the NM approximation no reasonable correspondence can be found between the theoretical and experimental values. Since, by and large, this is also the case for the other methods described in Table 4, the PP approximation seems undoubtedly much better than the NM for the calculation of spin densities.

Finally, it should be noted that the above excellent agreement obtained with the PP approximation is lost if $Q^{\mathrm{H}}_{\mathrm{CH}}$ values inclusive of their variations with the bond angle[30] are used in place of the above value of -23G. Although this is an interesting finding, we prefer to refrain from a presentation of detailed results and from detailed discussions;[31] here, we intend mainly to show the significance of the PP approximation through the use of the convenient formulas obtained.

The calculations have been carried out on the FACOM 230-60 computer at the Computer Center of Kyushu University.

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[31] Y. Gondo, M. Hirai, and Y. Kanda, to be published; M. Hirai, MS thesis submitted to Kyushu University, March, 1971.