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Two-Parameter ω-Technique for MO Calculations

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Abstracts

A two-parameter ω-technique for MO calculations is proposed. The parameters ω and ω' are chosen empirically to obtain a good agreement between calculated and observed bond lengths. The method amounts to an inclusion of the effect of nearest-neighbour electronic repulsion integrals into the conventional ω-technique.

Une technique ω avec deux paramètres pour des calculs de type MO est proposée. Les paramètres ω et ω' sont choisis d'une façon empirique pour obtenir un bon accord entre les longueurs de liaison calculées et observées. La méthode se réduit à l'inclusion de l'effet des intégrales de répulsion des plus proches voisins dans la technique ω conventionnelle.

Es wird ein Zweiparameter-ω-Verfahren für MO-Berechnungen vorgeschlagen. Die Parameter ω und ω' werden empirisch gewählt um gute Übereinstimmung zwischen berechneten und observierten Bindungslängen zu erhalten. Das Verfahren betragt eine Einschliessung der Effekte der elektronischen Abstossungsintegrale von den nächsten Nachbarn in das konventionelle ω-Verfahren.

1. Introduction

The ω-technique [1] is one of the simplest methods of taking into account the charge distribution in LCAO-MO calculations. It consists of modifying the Coulomb integral α at each centre by the π-electron density q_μ on that centre according to the relation,

$$\alpha_\mu = \alpha + (1 - q_\mu)\omega\beta \tag{1}$$

where ω is an empirically evaluated dimensionless parameter having a generally accepted value of 1.4 [2] and β is the resonance integral. A crude justification for the ω-technique may be obtained [3] by comparing Eq. (1) with the equations obtained in the Pariser–Parr–Pople (PPP) approximation [4, 5]. The latter equa-

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tions are

$$\varepsilon_i = \sum_{\mu} c_{i\mu}^2 \alpha_\mu + 2 \sum_{\mu<\nu} c_{i\mu} c_{i\nu} \beta_{\mu\nu} \tag{2}$$

$$\alpha_\mu = (\alpha_\mu)_{\text{core}} + \tfrac{1}{2} q_\mu (\mu\mu|\mu\mu) + \sum_{\nu\neq\mu} q_\mu (\mu\mu|\nu\nu) \tag{3}$$

$$\beta_{\mu\nu} = (\beta_{\mu\nu})_{\text{core}} - \tfrac{1}{2} p_{\mu\nu} (\mu\mu|\nu\nu) \tag{4}$$

where the symbols have their usual meaning. If the α and $\omega\beta$ of Eq. (1) are taken to be equal to $(\alpha_\mu)_{\text{core}} + \frac{1}{2}(\mu\mu|\mu\mu)$ and $-\frac{1}{2}(\mu\mu|\mu\mu)$, respectively, and the two centre repulsion integrals are neglected in Eq. (3), the two equations become exactly identical. Thus whatever differences appear between the results of the two methods will have arisen primarily due to the neglect of any contributions of the two-centre repulsion integrals to α and β. It would therefore be profitable if one could include in some way their effect in the ω-technique and yet retain the simplicity of the method.

In the past few years, several attempts [6–10] have been made in this direction, but a rigorous justification on the basis of a comparison of the equations used in them with the PPP equations cannot be obtained for these methods. As is obvious from Eqs. (3) and (4), if the two-centre electronic repulsion integrals are to be included, it would amount to establishing a dependence of the diagonal elements α_μ on electron densities at all the centres other than μ and of the off-diagonal elements $\beta_{\mu\nu}$ on the bond order $p_{\mu\nu}$. While the methods of Dorko et al. [6] and Huy and Forst [7] do consider this latter dependence, they ignore the dependence of the α_μ terms on electron densities at the centres other than μ. Grundler [8] has correctly included the dependence of α_μ terms on $q_\nu (\nu \neq \mu)$ but neglected altogether the dependence of $\beta_{\mu\nu}$. The method of Gupta and Krishan [9] and of Krishan et al. [10] are based on a relationship proposed by Harris [11], the consequence of which is an explicit dependence of α_μ not on the electron densities but on the bond orders between the site and all the other sites. Also the expression for $\beta_{\mu\nu}$ does not involve an explicit dependence on $p_{\mu\nu}$.

The present article outlines a procedure which makes use of the correct dependences for both α_μ and $\beta_{\mu\nu}$. The method is a simple extension of the conventional ω-technique and may appropriately be termed a two-parameter ω-technique, as it involves two empirical parameters instead of one.

2. Method

Let us write an equation analogous to Eq. (1) for $\beta_{\mu\nu}$ in the form

$$\beta_{\mu\nu} = \beta + (1 - p_{\mu\nu}) \omega'_{\mu\nu} \beta \tag{5}$$

It would represent a correction to the resonance integral due to the deviation of the corresponding bond order from its ethylene value (=1). Now let us rewrite Eq. (4) as

$$\beta_{\mu\nu} = \{(\beta_{\mu\nu})_{\text{core}} - \tfrac{1}{2}(\mu\mu|\nu\nu)\} + (1 - p_{\mu\nu}) \tfrac{1}{2}(\mu\mu|\nu\nu) \tag{6}$$

Comparing Eqs. (5) and (6) we get

$$\beta = (\beta_{\mu\nu})_{\text{core}} - \tfrac{1}{2}(\mu\mu|\nu\nu)$$

and

$$\omega'\beta = \tfrac{1}{2}(\mu\mu|\nu\nu)$$

Now let us invoke the Huckel approximation for resonance and overlap integrals, i.e., $\beta_{\mu\nu} = 0$ for μ and ν nonbonded and $S_{\mu\nu} = \delta_{\mu\nu}$.

Now we need consider only nearest-neighbour two centre repulsion integrals. Then for homomolecules, $\omega'_{\mu\nu}$ will be limited to a single parameter ω'. Under these conditions Eqs. (3) and (5) reduce to

$$\alpha_\mu = \alpha + (1-q_\mu)\omega\beta - \sum_{\nu \text{ bonded to } \mu} (1-q_\nu)2\omega'\beta \tag{7}$$

$$\beta_{\mu\nu} = \beta + (1-p_{\mu\nu})\omega'\beta \tag{8}$$

with

$$\omega/\omega' = -(\mu\mu|\mu\mu)/(\mu\mu|\nu\nu) \tag{9}$$

and

$$\alpha = (\alpha_\mu)_{\text{core}} + \tfrac{1}{2}(\mu\mu|\mu\mu) + \sum_{\nu \text{ bonded to } \mu} (\mu\mu|\nu\nu) \tag{10}$$

Since both $(\mu\mu|\mu\mu)$ and $(\mu\mu|\nu\nu)$ are positive, according to Eq. (9), ω and ω' should have opposite signs. The value of $(\mu\mu|\mu\mu)$ for the carbon atom turns out to be 10.84 eV from Pritchard and Skinner's data [12] on valence-state ionization potential and the value of $(\mu\mu|\nu\nu)$ for the ethylene bond (1.335 Å) [13] is 5.41 eV from the Nishimoto–Mataga formula [14]; hence the magnitude of ω' is expected to be about half that of ω. For the generally adopted value of $\omega = 1.4$ [2], ω' should then be somewhere near -0.7. However in the present work an attempt has been made to optimize the values of the two parameters within a wide range although the final set of values has come out exceptionally close to the above choice.

3. Numerical Calculations and Results

To allow a comparison, the same small ring unsaturated hydrocarbons as those chosen by Dorko et al. [6] have been chosen for numerical study. In addition, linear polyacenes, for which much theoretical and experimental data is available, have been included in the present calculations. The calculations were performed on an ICL 1909 computer. For diagonalization of matrices Jacobi's method [15] was used, a word of caution about which is not perhaps out of place at this point. The original Jacobi technique does not make any reference to the ordering of eigenvalues. Therefore, before filling the MOS with electrons followed by calculation of electron densities and bond orders, one should make sure that the energy levels are in fact arranged in a descending order.

In the present work, a convergence of 0.001 in electron densities and bond orders has been sought. To accelerate the process an averaging procedure given by Mathur and Singh [16] has been used. None of the molecules studied required more than 18 iterations to achieve the desired self-consistency. However, for the smaller molecules picked from Dorko's list the maximum number of iterations required was only 12. Parametrization for ω and ω' has been tried in the range of 1.0 to 2.0 for ω and 0.0 to -1.0 for ω'. It has been found that the results are very sensitive to the choice of ω', but not equally sensitive to the choice of ω. Performance of different sets of ω, ω' values has been judged by comparing the closeness to linearity of the correlation between calculated bond orders and the experimentally determined bond lengths for butadiene, trimethylene cyclopropane, and the linear polyacenes up to tetracene (Fig. 1). To put a further check on the values of ω and ω' similar calculations were carried out for the ionization potentials and $V1 \leftarrow N$ transition frequencies for the various linear polyacenes up to pentacene. One constraint on the bond length–bond order correlation line is that it should be exactly satisfied by the ethylene bond (bond length = 1.335 Å, bond order = 1). Thus it has been found that the best correlation results for $\omega' = -0.6$ and values of ω varying from 1.0 to 1.6. However, to keep in conformity with the generally accepted value of ω, the final values for the parameters have been chosen as $\omega = 1.4$ and 0.6. The least squares correlation line between bond

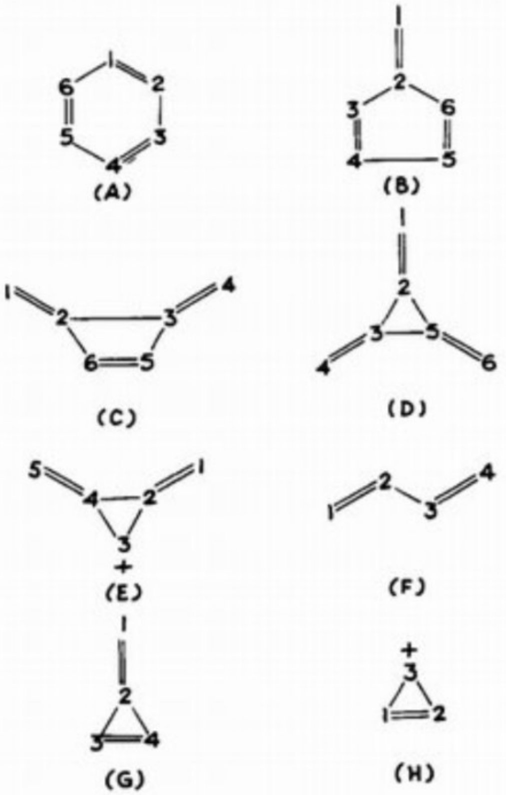

Figure 1. Numbering of atoms in the molecules: (A) benzene, (B) fulvene, (C) dimethylene cyclobutene, (D) trimethylene cyclopropane, (E) dimethylene cyclopropanyl, (F) butadiene, (G) methylene cyclopropane, (H) cyclopropenyl.

length and bond order for this set of parameters is

$$\gamma_{\mu\nu} = -0.183 p_{\mu\nu} + 1.521 \tag{11}$$

The calculated charge densities, bond orders, and bond lengths are presented in Table I. A comparison of the calculated bond lengths with the experimentally observed, as well as with those calculated by other workers, for the six molecules

TABLE I. Molecular parameters calculated by the two-parameter ω-technique.

Atom position	Electron density	Bond	Bond order	Bond length (Å)
Benzene	1.000	1–2	0.667	1.399
1				
Fulvene				
1	0.948	1–2	0.918	1.353
2	0.980	2–3	0.278	1.470
3	1.034	3–4	0.914	1.354
4	1.002	4–5	0.308	1.465
Dimethylene Cyclobutene				
1	1.000	1–2	0.945	1.348
2	1.000	2–3	0.213	1.482
3	1.000	2–6	0.246	1.476
		5–6	0.923	1.352
Trimethylene Cyclopropane				
1	1.009	1–2	0.928	1.351
2	0.991	2–3	0.261	1.473
Dimethylene Cyclopropanyl	Cation			
1	0.655	1–2	0.796	1.375
2	0.129	2–3	0.529	1.424
3	0.432	2–4	0.168	1.490
	Radical			
1	1.045	1–2	0.814	1.372
2	0.980	2–3	0.512	1.427
3	0.950	2–4	0.219	1.481
	Anion			
1	1.429	1–2	0.810	1.373
2	0.840	2–3	0.495	1.430
3	1.463	2–4	0.249	1.475
Butadiene				
1	1.000	1–2	0.960	1.345
2	1.000	2–3	0.281	1.470
Methylene Cyclopropene				
1	1.106	1–2	0.941	1.349
2	1.008	2–3	0.238	1.477
3	0.943	3–4	0.943	1.348
Cyclopropenyl Cation				
1	0.667	1–2	0.666	1.399
2	0.667	1–3	0.667	1.399

for which the experimental results are available, is presented in Table II. Correlation of molecular energy levels with other properties (ionization potential and $V1 \leftarrow N$ transition) and a comparison with experimental data are presented in Tables III and IV.

TABLE II. Calculated and observed bond lengths.

Bond μ–ν	Bond order $p_{\mu\nu}$	Bond length (Å) $\gamma_{\mu\nu}$ PPP[a]	SPO[a]	Present calculations[b]	Experimental values
Benzene					
1–2	0.667	1.393	1.393	1.399	1.397[c]
Butadiene					
1–2	0.960	1.350	1.345	1.345	1.344[d]
2–3	0.281	1.456	1.464	1.470	1.464[d]
Trimethylene Cyclopropane					
1–2	0.928	1.349	1.346	1.351	1.343[e]
2–3	0.281	1.463	1.469	1.473	1.453[e]
Naphthalene[f]					
1–2	0.781	1.373	1.396	1.378	1.363
1–9	0.510	1.421	1.426	1.428	1.421
2–3	0.531	1.416	1.422	1.424	1.415
9–10	0.590	1.403	1.396	1.413	1.418
Anthracene					
1–2	0.822	1.369	1.362	1.370	1.366
2–3	0.472	1.422	1.432	1.435	1.419
1–13	0.450	1.428	1.437	1.439	1.434
13–14	0.520	1.412	1.409	1.426	1.428
Tetracene					
1–2	0.840	1.364	1.358	1.367	1.385
2–3	0.441	1.429	1.440	1.440	1.479
1–13	0.421	1.436	1.445	1.444	1.431
13–14	0.476	1.421	1.422	1.434	1.439
12–13	0.689	1.390	1.385	1.395	1.398
12–15	0.562	1.412	1.415	1.418	1.409
15–16	0.490	1.419	1.413	1.431	1.478

[a] M. J. S. Dewar and C. J. Gleicher, J. Am. Chem. Soc. **87**, 685, 692 (1965).
[b] $\gamma_{\mu\nu} = -0.18332p_{\mu\nu} + 1.52107$.
[c] B. P. Stoicheff, Can. J. Phys. **32**, 339 (1954).
[d] Ar. H. Cole, G. M. Mohay, and G. A. Osborne, Spectrochim. Acta **23A** 909 (1967).
[e] E. A. Dorko, J. L. Henscher, and S. H. Bauer, Tetrahedran **24**, 2425 (1968).
[f] Experimental values for naphthalene, anthracene, and tetracene obtained from Ref. (*a*).

4. Discussion

Table II shows that the two-parameter ω-technique predicts bond lengths not only in very good agreement with the experimental results but also that the overall results are superior to those predicted by the method of Dorko et al. [6].

TABLE III. Ionization potential (I.P.) for polyacenes calculated by different methods. (m_i = HOMO energy in units of β.)

Molecule	Present calculations (I.P. (eV) = $4.92m_i + 5.30$)	CNDO/S2 calculations (I.P. = −HOMO (eV)−0.8[a])	Experimental values[b]
Benzene	9.23	9.24	9.24
Naphthalene	8.15	8.06	8.15
Anthracine	7.44	7.40	7.40
Tetracine	6.98	7.00	7.01
Pentacene	6.65	6.74	6.64

[a] These values represent the least-squares fit between calculated and experimental values excluding pentacene. When pentacene is included, a closer fit is obtained for pentacene, however, the other values such as benzene and tetracene, diverge. In our case, the inclusion or exclusion of pentacene does not change the correlation line significantly.

[b] N. O. Lipari and C. B. Duke, J. Chem. Phys. **63** (5), 1768 (1975).

TABLE IV. Position of $V1 \leftarrow N$ electronic transition of polyacenes calculated by different methods. (Δm = (HOMO) − (LEMO).)

Molecule	Present calculations $= 29743\Delta m + 577$ (cm^{-1})	CNDO/S2 calculations $= 63160\Delta m - 9955$ (cm^{-1})	Experimental values[a] (cm^{-1})
Benzene	48166	48593	48400
Naphthalene	35097	34445	34700
Anthracine	26535	26235	26400
Tetracene	20903	21119	21200
Pentacene	17448	17708	17400

[a] S. C. Mathur and D. C. Singh, Ind. J. Pure Appl. Phys. **8** (12), 788 (1970).

Surprisingly enough, the results are also superior to the PPP results even though the former does not include the effect of nonneighbour electronic repulsion integrals. Results are also consistent with some recent CNDO/S2 calculations on the polyacenes [17].

Thus a simple extension of the conventional ω-technique has been presented here which makes use of two empirically chosen parameters and is capable of giving results consistent with those from more sophisticated SCF methods. However, before a universal set of values for ω and ω′ can be agreed upon, the method will have to be applied to a wide variety of molecules.

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