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A Semi-Empirical MO-Electron Correlation Method for Molecules and the Correlation Energies of π-System Linear and Polycyclic Hydrocarbons*

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A set of approximations referred to as the "EPCE-F2 Method" is presented starting from the MO-pair correlations theory by Sinanoğlu of ground state molecules. It yields estimates of the correlation energies using LCAO MO coefficients and one and two center pair correlation parameters. The method applied to π-systems yields explicit expressions for correlation energies in terms of the number of carbon atoms, π-bonds, and the number of rings. The π-correlation energies of polyenes and various types of polyacenes are given. Results are compared with available alternant MO (AMO) and π-CI calculations. Correlation energies per electron are also obtained as number of carbon atoms increase and approach the very large system limits like a layer of graphite.

Es wird ein als „EPCE-F2 Methode" bezeichneter Satz von Näherungen vorgeschlagen, der von der MO-Paarkorrelationstheorie für Moleküle im Grundzustand ausgeht. Die Methode liefert Näherungswerte der Korrelationsenergien, wobei die LCAO-MO-Koeffizienten und Ein- bzw. Zweizentren-Korrelationsparameter verwendet werden. Bei π-Elektronensystemen erhält man explizite Beziehungen für die Korrelationsenergien, die von der Anzahl der Kohlenstoffatome, der π-Bindungen und der Ringe ausgehen. Die π-Korrelationsenergien der Polyene und verschiedener Typen von Polyacenen werden angegeben und die Ergebnisse mit den zur Verfügung stehenden AMO-MO und π-CI Berechnungen verglichen. Auch die Korrelationsenergien pro Elektron werden in Abhängigkeit von der steigenden Anzahl der Kohlenstoffatome und für den Grenzfall sehr großer Systeme wie Graphitschichten mitgeteilt.

Introduction

The molecular orbital Hartree-Fock (MO HF) method gives the charge distribution related properties of singlet ground states well, but it does not account for dissociation energies, electron affinities and the like [1]. The F_2 molecule as an extreme case is predicted to be highly unstable with respect to 2F by rigorous Hartree-Fock MO results for example [2]. For energetics, the rest of the exact non-relativistic energy, i.e. electron correlation energy, E_{corr}, is needed.

MO-methods for large molecules, whether non-empirical or semi-empirical, formally start from the MO HF theory, but of necessity involve many approximations already at the HF MO level itself. The errors resulting from the difference between approximate MO-energies and actual HF energies are much larger than

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quantities of interest. The calculations of rigorous HF for molecules beyond diatomics and the smallest of polyatomics, remain a technically formidable problem. In addition, by and large, approximate MO-methods do not deal with electron correlation.

Since 1959, a theory of electron correlation suitable for large atoms and molecules has been developed both for ground (MET) [3], and for excited states, i.e. general non-closed shell states (NCMET) [4]. This theory by Sinanoğlu has predicted and shown that, difficult to calculate, "dynamical" correlation effects can be obtained semi-empirically transferring them between atomic and molecular states, [5, 6]. Other, "non-dynamical" correlations however have to be calculated in detail based on the theory as it has been done for atomic excited states [7].

In this paper, we first discuss several previous semi-empirical schemes for the E_{corr} of molecules. We then use some of the rigorous expressions which has been derived recently by Sinanoğlu for molecular pair correlations in the LCAO MO description [8]. We make further approximations on these to extend an initial early suggestion by Sinanoğlu to treat π-electron correlation energies in terms of one- and two-center, E_{pp} and E_{pq}, pair correlations [9]. We apply the results, to linear and polycyclic hydrocarbons to obtain the π-system [10] E_{corr}'s of the doubly occupied ground states explicitly in terms of the numbers of carbon atoms and rings in the molecule. The results are compared with limited basis π-CI and AMO (alternant MO) calculations in the literature.

Semi-Empirical Methods

Except for the "Pair Population Method" (PPM) of Hollister and Sinanoğlu [11], present empirical or semi-empirical methods may be used only for diatomic molecules or polyatomic hydrides. Hartree-Fock calculations [12] and a previous argument given by McKoy have shown that the united atom approach [14] overestimates the correlation energy. In the separated ion (SI) approach [14, 15], the total correlation energy of diatomic molecule is obtained from the correlation energies of the two atoms and their ions. One can use this approach only for diatomic molecules and central hydrides. In the "Shrunk–Core" model of Hollister and Sinanoğlu [11] outer MO electrons see a core which is quite like the cores of the constituent atoms. This model reduces to the united atom approach in the case of central hydrides, but it can predict the correlations energies of AH_nBH_m type molecules which the united atom cannot.

The "Pair Population Method", by contrast to the above, can be applied to any molecule as long as simple MO electron populations and atomic pair energies are known. The *correlation binding energy* is defined as the difference between the sum of the correlation energies of atoms in that molecule and the molecular correlation energy [6]. The correspondence between the correlation binding energies found by the PPM and the "experimental" ones [16] is excellent for small molecules. But the ratio of the estimated correlation binding energy to the experimental one decreases as the number of atoms in molecules increases [11].

It should be noted that PPM is based on the use of only the *gross atomic populations.* One converts these gross atomic populations into gross "pair populations" as defined in Ref. [11]. This allows one to express and obtain the E_{corr} (molecule) in terms of only the one-center, atomic pair correlations. The latter are given by MET [3]. In MO population analysis overlap populations are divided up and added onto *net populations* to get the *gross*. In the same way, implicit in PPM is the sub-division of the overlap region correlations among atoms and their addition to the purely one center ε_{pp} contributions. The study of this approximation requires more explicit expressions for the molecular E_{corr} suitable for a LCAO framework.

Sinanoğlu has derived rigorous LCAO-type expressions for molecular correlations and from these a number of different approximations applicable to both σ- and π-systems [8]. The use of zero differential overlap (ZDO)-like approximations on these expressions had led to his suggestion of a semi-empirical method in terms of one and two-center ε_{pp} and ε_{pq}-type pair correlations [9]. In the meanwhile, this suggestion has been developed to some extent with additional approximations and different contexts by Pamuk [17], by Brown and Roby [18], and by Labzowski [19]. We develop the ε_{pp}, ε_{pq}-method further here and apply it extensively to π-electron systems. The method is based on MET, i.e. only on the *ground state* correlation theory [3]. Thus it applies only to ground states. From it, one can also see what explicit approximations lead to PPM. For π-systems, even large polycyclics, the present one- and two-center method should yield better results.

The Ground State Molecular Correlation Energy in the LCAO Form for π-Systems

Theory of electron correlation in doubly occupied ground states shows that [3]

$$E_{\text{corr}} \cong \sum_{i>j\geq 1}^{N} \varepsilon_{ij}\,, \tag{1}$$

where $i,j \in \{1,2,\ldots,N\}$ are occupied HF MO spin-orbitals and ε_{ij} are the MO-pair correlations of MET. These are in the spin-orbital form, further they are the "*total*" ε_{ij}'s of the MET-type [3], $\varepsilon_{ij}^{\mathrm{T}}$. In the more detailed NCMET (applicable to excited states and which rigorously reduces to MET in the closed shell limit) one would have [1, 6]

$$\varepsilon_{ij}^{\mathrm{T}} = \varepsilon_{ij}^{\mathrm{INT}} + \varepsilon_{ij}^{\mathrm{F}} + \varepsilon_{ij}^{\text{all-ext.}} \tag{2}$$

with the "internal" (INT), "semi-internal" (F), and "all-external" (all-ext) parts. For closed shells, one gets

$$\varepsilon_{ij} = \varepsilon_{ij}^{\mathrm{T}} = \varepsilon_{ij}^{\text{all-ext.}}\,. \tag{3}$$

The ground states of π-systems are not closed, but "quasi-closed" shells (doubly occupied, single det HF). Thus the ε_{ij}'s pertinent to the present paper are in general of the $\varepsilon_{ij} = \varepsilon_{ij}^{\mathrm{T}}$-type, Eq. (2).

From Eq. (1), Sinanoğlu has obtained [8] the spinless forms of E_{corr} and in the LCAO-form. Upon further making ZDO-type approximations for π-systems (invariant only for π-systems), he gets

$$\boxed{\begin{aligned} E_{\mathrm{corr}} \underset{(\pi)}{\cong} \tfrac{1}{4} & \sum_{\substack{\mu,\nu \\ (\mu\neq\nu)}} (P_{\mu\mu}P^{*}_{\nu\nu} + |P_{\mu\nu}|^2)\,\varepsilon(\mu^{\alpha}\nu^{\beta}) \\ & + \tfrac{1}{4} \sum_{\substack{\mu,\nu \\ (\mu\neq\nu)}} (P_{\mu\mu}P^{*}_{\nu\nu} - 2|P_{\mu\nu}|^2)\,\varepsilon(\mu^{\alpha}\nu^{\alpha}) \\ & + \tfrac{1}{4} \sum_{\mu} |P_{\mu\mu}|^2\,\varepsilon(\mu^{\alpha}\mu^{\beta})\,. \end{aligned}} \tag{4}$$

The μ, ν are the spinless π-atomic orbitals (AO). $P_{\mu\nu}$ is the usual AO-density matrix

$$P_{\mu\nu} = 2 \sum_{k}^{N/2} c_{\mu}^{k} c_{\nu}^{k*} \tag{5}$$

in terms of the π-spinless MO(k), LCAO coefficients c_{μ}^{k}.

The $\varepsilon(\mu^{\sigma}\nu^{\sigma'})$ are related to the ε_{ij} of Eq. (1) and are given by (cf. Ref. [6])

$$\varepsilon(\mu^{\sigma}\nu^{\sigma'}) = \langle B(\mu^{\sigma}\nu^{\sigma'})|g_{12}|\hat{u}(\mu^{\sigma}\nu^{\sigma'})\rangle \tag{6}$$

with $\hat{u}(\mu^{\sigma}\nu^{\sigma'})$, a AO-AO′ pair correlation function dependent on $\sigma\sigma'$ being $\alpha\beta$ or $\alpha\alpha$. The $\hat{u}$ are "orbital-orthogonal" rigorously, now to all the AO's, as in the original form of the theory [3, 6].

$$\langle \hat{u}(\mu^{\sigma}\nu^{\sigma'})|\lambda\rangle_{\vec{r}_1} = 0; \quad \lambda \in \{\text{all AO's, } \sigma \text{ and } \pi\}\,. \tag{7}$$

In Eq. (4) for π-systems, all multi-center cross-terms [6] have been neglected as for planar π-systems (excluding triple bonds) there are no one center cross terms anyway. However unlike in the MO-theory ZDO, here, two center exchange-terms which due to the difference of $\varepsilon(\mu^{\alpha}\nu^{\beta})$ and $\varepsilon(\mu^{\alpha}\nu^{\alpha})$, have been retained. In a correlation approximation strictly analogous to ZDO, one would have

$$\varepsilon(\mu^{\alpha}\nu^{\beta}) \underset{(\text{full ZDO-like})}{\cong} \varepsilon(\mu^{\alpha}\nu^{\alpha})\,. \tag{8}$$

In that case Eq. (8) substituted in (4) would yield [8]

$$\boxed{\begin{aligned} E_{\mathrm{corr}} \underset{\substack{(\pi) \\ (\text{full ZDO-like})}}{\cong} & \sum_{\mu>\nu\geqq 1}^{(\text{all } \pi \text{ AO})} (P_{\mu\mu}P^{*}_{\nu\nu} - \tfrac{1}{2}|P_{\mu\nu}|^2)\,e^{\mu\nu} \\ & + \tfrac{1}{4} \sum_{\mu\geqq 1}^{(\text{all } \pi \text{ AO})} |P_{\mu\mu}|^2\,e^{\mu\mu}\,. \end{aligned}} \tag{9}$$

where

$$e^{\mu\nu} \equiv \varepsilon^{\mu^{\alpha}\nu^{\beta}} \underset{(\text{full ZDO})}{\cong} \varepsilon^{\mu^{\alpha}\nu^{\alpha}},$$

and

$$e^{\mu\mu} \equiv \varepsilon^{\mu^{\alpha}\mu^{\beta}}\,.$$

However, except for large internuclear distances where $e^{\mu\nu}$ reduces to the usual Van-der Waals dispersion attractions [20, 6], there is no reason to expect Eq. (8) to hold. In atoms the $\varepsilon(\alpha\alpha)$ and $\varepsilon(\beta\beta)$ differ appreciably [3, 6].

One can then either use different values [8] for $\varepsilon(\mu^\alpha\nu^\beta)$ and $\varepsilon(\mu^\alpha\nu^\alpha)$ in Eq. (4) in a semi-empirical method at the usual π-bond distances, or replace Eq. (8), by what may be a more reasonable approximation. Pamuk [17, 21], and independently but for a different purpose, i.e. to reparametrize σMO-theory itself, Brown and Roby [18] have implicitly used [22] such a different approximation which also simplifies Eq. (4) more than Eq. (9). This approximation which we shall refer to as the "Factor Two (F2)-Approximation" is

$$\varepsilon(\mu^\alpha\nu^\beta) \underset{(\mathrm{F2})}{\cong} 2\varepsilon(\mu^\alpha\nu^\alpha)\,. \tag{10}$$

Substitution of Eq. (10) in Sinanoğlu's Eq. (4) above yields

$$\boxed{\begin{aligned} E_{\mathrm{corr}} \overset{(\mathrm{F2})}{\underset{\pi}{\cong}} \tfrac{1}{4} &\sum_{\substack{\mu,\nu\\(\mu\neq\nu)}} P_{\mu\mu}P^*_{\nu\nu}\bar{\varepsilon}_{\mu\nu} \\ &+\tfrac{1}{4}\sum_{\mu}|P_{\mu\mu}|^2\,\varepsilon(\mu^\alpha\mu^\beta) \end{aligned}}_{(\mathrm{F2})} \tag{11a}$$

where

$$\bar{\varepsilon}_{\mu\nu} \equiv \varepsilon(\mu^\alpha\nu^\beta) + \varepsilon(\mu^\alpha\nu^\alpha)\,. \tag{11b}$$

Thus $\bar{\varepsilon}_{\mu\nu}$ with the bar $(-)$ is the sum of $(\alpha\beta)$ and $(\alpha\alpha)$ pair correlations and was defined by Pamuk as an "effective pair energy" [17]. In the F2-approximation $\bar{\varepsilon}_{\mu\nu}$ strictly would become $(3/2)\,\varepsilon(\mu^\alpha\nu^\beta)$ due to Eq. (10). However, since neither $\varepsilon(\alpha\beta)$ nor $\varepsilon(\alpha\alpha)$ values are available as a function of internuclear distance *a priori*, $\bar{\varepsilon}_{\mu\nu}$ is derived semi-empirically and may be considered as a parameter in the (F2) context as such.

Eq. (11a) simplifies the two center terms eliminating P_{pq} $(p\neq q)$, while one center terms remain unchanged, as the π-systems considered in this paper have only one π-AO per center.

There are two primary input parameters in the "F2-method" which is the main concern of this paper, Eq. (11). These are 1) the two center $\pi\mathrm{AO}-\pi\mathrm{AO}'$ effective $(\alpha\beta+\alpha\alpha)$ pair correlation value $(\bar{\varepsilon}_{\mu\nu})$, and the one-center $\varepsilon(2p_z^2)$ (cf. Ref. [23]).

Evaluation of the One- and Two-Center MET-Type "Effective Pair Correlation Parameters" for Planar π-Systems

The two-center correlation energies depend on the internuclear distance, R_{pq}, as well as the atomic orbitals to which they belong. The Hydrogen molecule is one system whose correlation energy has been studied extensively in a large internuclear distance-range [24]. The absolute value of the correlation energy of this system remains almost constant up to the equilibrium distance, then rapidly decreases with increasing distance. Let us assume that the π two-center "effective pair energies" behave similarly, and can be represented by an equation:

$$\bar{\varepsilon}_{pq} = \tfrac{1}{2}(\bar{\varepsilon}_{pp} + \bar{\varepsilon}_{qq})\,f(R_{pq}, p, q) \tag{12}$$

for the internuclear distances larger than the equilibrium distance. The function f can be fitted to the correlation energy values estimated from the empirical Pariser-Parr γ_{pq} parameters using the detailed analysis of these parameters given by Sinanoğlu and Orloff [9]. For this, in the present F2-method, Pamuk [17] interprets the empirical two-center Pariser-Parr parameter γ'_{pq} as

$$\gamma'_{pq} \underset{(\mathrm{F2})}{=} \gamma^{\mathrm{HF}}_{pq} + \bar{\varepsilon}_{pq} \,. \tag{13}$$

This identification of γ'_{pq} (empirical) depends on which E^{π}_{corr} approximation is used along with the HF MO, ZDO approximation and how the semi-empirical E^{π}_{corr} expression is combined term by term with the E^{π}_{HF} (ZDO), i.e. the Pariser-Parr-Pople expression, [8], in

$$E^{\pi} = E^{\pi}_{\mathrm{HF}}(ZDO) + E^{\pi}_{\mathrm{corr}} \,. \tag{14}$$

Pamuk [17], and Brown and Roby [18, 25] have given forms which put some correlation also in the one-electron MO-matrix elements H'_{pq}. Sinanoğlu [8], in different approximations, adds the E^{π}_{corr} to the two-electron HF MO matrix elements only, this being closer to the rigorous formalism of electron correlation theory [3]. The F2-method here, nevertheless dictates the use of the form [17] given by Eq. (13).

Coming back to the evaluation of Eq. (12), we note that for $R_{pq} \to 0$, $f(R_{pq}) \to 1$, i.e. $\bar{\varepsilon}_{pq} \to \varepsilon(p^{\alpha} p^{\beta})$.

a) The One-Center Parameter

Empirically one-center Coulomb repulsion parameters are obtained from the Pariser formula [26]. Considering the valence state carbon charge transfer reaction

$$\dot{\mathrm{C}} + \dot{\mathrm{C}} \to \mathrm{C}^{+} + \ddot{\mathrm{C}}^{-} \tag{15}$$

Pariser used

$$\gamma'_{pp} = I_C - A_C \,, \tag{16}$$

where I_C and A_C are valence state ionization potential and valence state electron affinity, respectively.

The HF energy change, ΔE_{HF}, for the reaction in Eq. (15) and the energy change, $\Delta E^{\mathrm{orbital}}_{\mathrm{HF}}$, due to the changes in the σ and π orbitals have been calculated by Sinanoğlu and Orloff [9]. Then the HF Coulomb parameters were obtained from

$$\gamma^{\mathrm{HF}}_{pp} = \Delta E_{\mathrm{HF}} - \Delta E^{\mathrm{orbital}}_{\mathrm{HF}} \,. \tag{17}$$

Finally using Eq. (13) they found $\bar{\varepsilon}_{pp} = -1.09$ eV (for one center $\bar{\varepsilon}_{pp} = \varepsilon(p^{\alpha} p^{\beta})$).

b) The Two-Center Parameter

The semi-empirical π-electron theory has been fitted to the spectroscopic states of benzene to obtain empirical parameters for use in π-systems [27]. The resulting two-center empirical γ'_{pq} $(p \neq q)$ are $\gamma'_{00} = 11.35$ eV, $\gamma'_{01} = 7.19$ eV, $\gamma'_{02} = 5.77$ eV, and $\gamma'_{03} = 4.97$ eV. Assuming these parameters can be represented by a continuous function of the internuclear distance, R_{pq}, the following poly-

Table 1. Coulomb repulsion integrals for π-system carbon valence state-like Hartree-Fock orbitals and the two-center effective correlation parameter, $\bar{\varepsilon}_{pq}(=\varepsilon_{pq}(\alpha\beta)+\varepsilon_{pq}(\alpha\alpha))$

R_{pq}	$\gamma_{pq}^{\mathrm{HF}}$ (eV)	γ'_{pq} (eV)	$-\bar{\varepsilon}_{pq} \equiv (\gamma_{pq}^{\mathrm{HF}} - \gamma'_{pq})$ (eV)
0.0	11.69[a]	10.60[a]	1.09[a]
[0.0	12.889[b]	11.35[c]	1.539]
1.390	8.008	7.199	0.809
1.397	7.984	7.190	0.794
1.400	7.974	6.186	0.788
1.600	7.321	6.924	0.397

[a] From Ref. [9] in text.
[b] See section after Eq. (18) in text.
[c] Ref. [27] and Eq. (18).

nomial is fitted:

$$\gamma'_{pq} = -0.425_7 R_{pq}^3 + 2.281_1 R_{pq}^2 - 5.333_7 R_{pq} + 11.35\,. \tag{18}$$

It has been pointed out by Sinanoğlu and Orloff [9] that the Roothaan open shell HF $2p_z$ atomic orbital of $(1s^2\,2s\,2p^4, {}^4P)$ of C^- is very close to the valence state average HF orbital occuring in the C^- valence state. We calculated the two-center Coulomb repulsion integrals using the diatomic integral program of Corbato and Switendick [29] for several internuclear distances around the experimental bond distances of benzene ($R_e = 1.397$ Å) with Hartree-Fock orbitals [28]. The results are given in the second column of Table 1. The empirical Coulomb repulsion parameters, given in the third column, are obtained from the polynomial in Eq. (18). The differences between the two calculations are listed in the last column. The Pamuk value [17] for the one-center $\gamma_{pp}^{\mathrm{HF}}$ indicates that both $\gamma_{pp}^{\mathrm{HF}} = 12.889$ eV and the present empirical γ'_{00} differ from the earlier results [9], probably because this $\gamma_{pp}^{\mathrm{HF}}$ does not include the energy change due to the change in the σ and π orbitals. We shall use the more accurate, older ε_{pp}. The trend of $(\gamma_{pp}^{\mathrm{HF}} - \gamma'_{pq})$ shows that the two-center correlation energy between non-neighboring atoms is very small and can be neglected. Identification of the $(\gamma'_{pq} - \gamma_{pq}^{\mathrm{HF}})$ according to the F2-approximations here, Eqs. (13) and (11b) yields the effective $\bar{\varepsilon}_{pq}$ values. In this paper the Pamuk [17] values for $\bar{\varepsilon}_{pq}$ in Table 1 will be used for $p \neq q$ although probably a better set of values can be derived from a more complete use of MET. The results in the next section for various molecules are given in such a way that even if a different $\bar{\varepsilon}_{pp}$ value were used in the future, the results would still be valid, only a proportionality factor changing.

π-System Correlation Energy as a Function of the Number of Atoms and of Rings in a Molecule

The smallness of the $\bar{\varepsilon}_{pq}$ values for non-nearest neighbor p, q's allows us to write E_{corr}^{π}, Eq. (11a) in the nearest neighbor (n.n.) approximations, as

$$E_{\mathrm{corr}}^{\pi}(\mathrm{n.n.}) = \tfrac{1}{4} \sum_{p \geqq 1}^{N_\pi} P_{pp} \{P_{pp}\bar{\varepsilon}_{pp} + P_{(p+1)(p+1)}\bar{\varepsilon}_{p(p+1)} + P_{(p-1)(p-1)}\bar{\varepsilon}_{p(p-1)}\}\,. \tag{19a}$$

This equation is for those planar π-systems in which every π-center has at most two π-center nearest neighbors. For linear systems, polyenes $P_{00} = P_{(N_\pi+1)(N_\pi+1)} = 0$. For monocyclics $P_{00} = 0$ and $P_{(N_\pi+1)(N_\pi+1)} = P_{11}$, i.e. the addition $(n_\pi + m)$ is modulo N_π.

For more general planar topologies with possibility of more than two nearest-neighbors, e.g. polycyclic aromatics we have

$$E^{\pi}_{\text{corr}}(\text{n.n.}) = \tfrac{1}{4} \sum_{p \geqq 1}^{N_\pi} P_{pp} \left\{ P_{pp}\bar{\varepsilon}_{pp} + \sum_{\substack{q \\ (q \neq p)}}^{m(p)} P_{qq}\bar{\varepsilon}_{pq} \right\}. \tag{19b}$$

For each p, the q runs over all nearest neighbors of which there are $m(p)$.

For planar hydrocarbons all one-center π effective pair energies are equal. Since the bond lengths do not vary much, we shall assume that $f(R_{pq})$, in Eq. (12), also does not change considerably for the distances around the equilibrium bond length and further that the two-center effective pair energies are proportional to values that may be taken for the one-center ones:

$$\bar{\varepsilon}_{pp(+1)} \cong \bar{\varepsilon}_{p(p-1)} \cong k\bar{\varepsilon}_{pp} \,. \tag{20}$$

In general, the charge order (or electron population) on atom p is very close to one. Since the sum of the electron populations is equal to the number of electrons, if we denote $P_{pp} = 1 - \delta_p$, the sum of the δ_p vanishes:

$$\sum_p \delta_p = 0 \,. \tag{21}$$

With the help of Eqs. (20) and (21) and neglecting the terms like δ_p^2 or $\delta_p\delta_q$, Eq. (19) can be written as

$$E^{\pi}_{\text{corr}}(\text{n.n.}) \cong \tfrac{1}{4}\bar{\varepsilon}_{pp}(\nu + 2kB) \,, \tag{22}$$

where ν is the number of the π-electron contributing atoms in the molecule, (it is assumed that each atom contributes only one $2p$ electron); B is the number of the C–C bonds between C-atoms each contributing a π-electron, and $k = \bar{\varepsilon}_{pq}/\bar{\varepsilon}_{pp}$ (only for neighboring atoms).

B can be expressed in terms of the number of rings, ϖ, and the number of atoms, ν:

$$B = \nu + \bar{\omega} - 1 \,. \tag{23}$$

Then the correlation energy expression becomes:

$$\boxed{E^{\pi}_{\text{corr}}(\text{n.n.}) \cong \tfrac{1}{4}\bar{\varepsilon}_{pp}[(1 + 2k)\nu + 2k\bar{\omega} - 2k]}_{\text{(F2)}} \tag{24}$$

Assuming $\bar{\varepsilon}_{pp} = -1.09$ eV and $\bar{\varepsilon}_{pq} = -0.79$ eV, we obtain $k = 0.7284$ and

$$E^{\pi}_{\text{corr}}(\text{n.n.}) \underset{\text{(in eV)}}{\cong} 0.397 - 0.669\nu - 0.397\bar{\omega} \,. \tag{25}$$

Rather than Eq. (25), the Eq. (24) is of course more significant since there could be different values of $\bar{\varepsilon}_{pp}$ and k used. On the other hand one could also extract the $\bar{\varepsilon}_{pp}$ and k values, if one had sufficiently complete non-empirical E^{π}_{corr} values for a set of molecules after testing their ν and $\bar{\omega}$-dependence.

In the following section we shall apply the above equations (especially Eq. (25)) to various types of planar π-molecules. In comparing the above equations with CI calculations on π-systems in the literature it needs to be kept in mind that our equations like Eq. (25) refer to the total E^{π}_{corr}, i.e. including the "internal", "semi-internal", and "all-external" correlations as in MET, Eq. (2). On the other hand, what is usually referred to as "full CI", e.g. for the benzene π-system in the literature, corresponds to CI with all the dets that can be formed from the $2p_{\pi}$-orbitals only. Thus "full CI" in that sense is only the "internal correlation" E_{int} of NCMET [30].

Also one may note that in the present semi-empirical E^{π}_{corr}, we have assumed that the "decoupled" or at least some type of transferable effective pair correlations suffice as predicted by MET [3, 20] and found to be true recently for many atoms and molecules by many workers [31, 3c]. However, MET also makes allowance for the calculation of three and more electron correlation remainders [3], R', which are in fact dominant in the other extreme of the uniform infinite electron gas [31]. Thus although still at benzene pair correlations seem quite adequate, it remains to be studied by non-empirical MET-CI procedures [3, 31] to what extent this is true in larger systems approaching a layer of graphite.

Applications

a) Linear Chains-Polyenes

Since $\bar{\omega} = 0$, Eq. (25) takes a simpler form:

$$E^{\pi}_{\mathrm{corr}}(\mathrm{n.n.}) \cong \tfrac{1}{4}\bar{\varepsilon}_{pp}[(1+2k)\nu - 2k]_{\mathrm{F2}}\,, \tag{26a}$$

or

$$E^{\pi}_{\mathrm{corr}}(\mathrm{n.n.}) \cong 0.397 - 0.669\nu \quad (\mathrm{in\ eV})\,. \tag{26b}$$

In Table 2 correlation energies obtained by the present effective pair correlation energy method (EPCE)-F2, are compared with the CI and best AMO results. For ethylene Eq. (26) gives only 84% of the correlation energy obtained by CI or AMO methods [32], but then this is subject to the lower $\bar{\varepsilon}_{pp}$ we used. In the case of butadiene, the correlation energy found by the EPCE-F2 method agrees very well with a CI treatment [33]. The AMO value for butadiene is smaller [34]. The slope of Eq. (26) gives the correlation energy per electron in the infinite chain.

Table 2. Correlation energies in electron volts of linear chains, E^{π}_{corr} of polyenes, as compared with CI and AMO

ν	CI[a]	AMO[a]	MET-EPCE-F2 (this work)
(Ethylene) 2	−1.127	−1.120	−0.941
(Butadiene) 4	−2.200	−1.746	−2.279
$\left[\lim_{\nu\to\infty} (E^{\pi}_{\mathrm{corr}}/\nu)\right.$	—	—	$\left.-0.669\ \mathrm{eV}\right]$

[a] See Refs. in Sect. Applications a) of text.

Table 3. π-System correlation energies (in eV) of quasi-linear cyclic hydrocarbons and comparison with CI and AMO

Number of atoms		$-E^{\pi}_{\text{corr}}$ (eV)				$-E^{\pi}_{\text{corr}}/\nu$ (eV)	
	ν	MET-EPCE-F2	AMO[a]	(in text Eq. (30))	CI[a]	MET-EPCE-F2	AMO[a]
(Benzene)	6	4.014	3.696	3.78	3.054	0.669	0.616
((Naphthalene)	10	7.088	6.732	6.73	—	0.709	0.673
(Anthracene)	14	10.161	9.653	9.62	—	0.726	0.690
⋮	18	13.234	12.465	12.54	—	0.735	0.693
(Infinitely long)	∞	—	—	—	—	0.768	0.7

[a] See Refs. in Sect. Applications b) of text.

b) Quasi-Linear Polycyclics

In these polyacenes, except the extreme ones, every ring has two neighboring rings. There is a simple relation between the number of atoms, ν, and the number of rings, $\bar{\omega}$:

$$\bar{\omega} = \tfrac{1}{4}(\nu - 2). \tag{27}$$

Substituting Eq. (27) into Eq. (24) yields an equation:

$$E^{k}_{\text{corr}}(\text{n.n.}) \cong \tfrac{1}{4}\bar{\varepsilon}_{pp}[(\tfrac{5}{2}k + 1)\nu - 3k]_{\text{F2}} \tag{28}$$

or using again $\bar{\varepsilon}_{pp} = -1.09$ eV and $k = 0.728$,

$$E^{\pi}_{\text{corr}}(\text{n.n.}) \cong 0.5955 - 0.768\nu \quad (\text{eV}) \tag{29}$$

which is again a linear function of the number of π-electrons or atoms, ν. The total correlation energies and the correlation energies per electron obtained from Eq. (29), and the many parameter AMO results [35] are tabulated in Table 3. Unfortunately, CI calculations for larger systems are very difficult. $E^{\pi}_{\text{corr}} = -3.05$ eV obtained by a 22×22 CI treatment is only a portion of the total correlation energy of the π-electrons in benzene [36]. The EPCE-F2 results are constantly larger in absolute magnitudes than the AMO values. This is reasonable because these non-empirical calculations are approximations only to some of the correlation effects. The AMO results are approximately reproduced (see Table 3) if Eq. (29) is rewritten as:

$$E^{\pi}_{\text{corr}}(\text{AMO}) = 0.6 - 0.733\nu \quad (\text{eV}). \tag{30}$$

c) Correlation Energy Per Electron in Very Large Systems

Let us assume there exists a very large molecule as in Fig. 1, in which every ring has three neighboring rings. From Eq. (25) we expect that the limit value of the correlation energy per electron will be larger in magnitude than the one found for quasi-linear cyclic systems. Indeed the number of the rings in this system can be expressed in terms of the number of atoms as (cf. Fig. 1)

$$\bar{\omega} = \tfrac{1}{3}(\nu - 4). \tag{31}$$

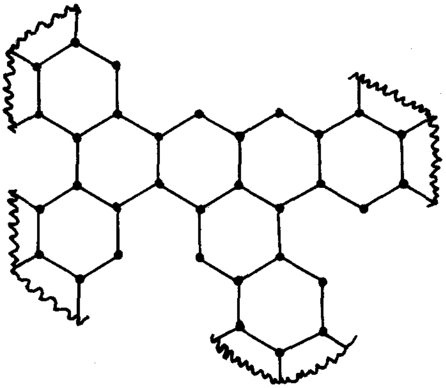

Fig. 1. A large molecule in which every ring has three neighboring rings

Then the total correlation energy is approximately

$$E^{\pi}_{\text{corr}} \cong 1.730 - 1.002\,v \quad (\text{eV}) \tag{32}$$

and

$$\lim_{v\to\infty}\left(\frac{E^{\pi}_{\text{corr}}}{v}\right) = -1.002 \quad (\text{eV})\,. \tag{33}$$

An estimation of the correlation energy per electron in a graphite-like layer is also possible. Let us pick a ring as the center, and draw circles as shown in Fig. 2. If we take n as the number of the circles, B, v, and $\bar{\omega}$ can be written as follows:

$$B = 6\left[4 \sum_{i \geqq 1} (i) + 1\right] \tag{34a}$$

$$v = 6\left[\sum_{i \geqq 1} (2i+1) + 1\right] \tag{34b}$$

$$\bar{\omega} = 6\left[\sum_{i \geqq 1} (i) + \tfrac{1}{6}\right]. \tag{34c}$$

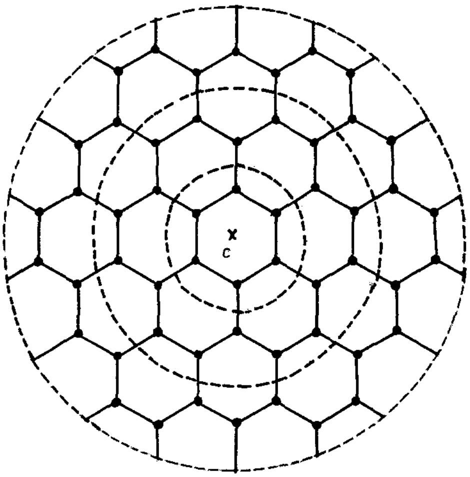

Fig. 2. A layer of graphite

The number of the bonds, B, can also be expressed as

$$B = 2v - 12n - 6 . \tag{35}$$

From Eqs. (22) and (35) or Eqs. (25) and (34), we obtain

$$E^{\pi}_{\mathrm{corr}}(\mathrm{n.n.}) = 2.382 - 4.764n - 1.066v \quad (\mathrm{eV}) \tag{36}$$

which yields

$$\lim_{v \to \infty} \left(\frac{E^{\pi}_{\mathrm{corr}}}{v} \right) = -1.066 \quad (\mathrm{eV}) . \tag{37}$$

Since the interactions between the layers are not included, the absolute value of the correlation energy per electron in graphite must be larger than 1.066 eV.

d) Cyclic H_6 *Molecule*

Although this molecule does not have π-electrons, theoretically, it can be treated like benzene. Its correlation energy, for $R = 2$a.u. separation, is calculated by a 9×9 CI and found to be $E_{\mathrm{corr}} = -2.058$ eV [37]. The AMO calculation has been rather unsuccessful for this molecule, giving only a small portion of the correlation energy [38]: $E_{\mathrm{corr}} = -1.272$ eV. In the united atom approach, the correlation energy of this system would be an average of $E_{\mathrm{corr}}(^1S, \mathrm{carbon}) = -5.415$ eV and $E_{\mathrm{corr}}(^1D, \mathrm{carbon}) = -4.6$ eV. Therefore, we expect a higher absolute value of the correlation energy for the H_6 ring to be about 4.5 eV. Neglecting the interactions between molecules, we assume that a lower absolute value of E_{corr} should be about three times the absolute value of the correlation energy for the Hydrogen molecule, i.e. 3.18 eV. At the 2 a.u. internuclear distance the two-center correlation energy for the H_2 molecule is -0.82 eV [24]. Using $\bar{\varepsilon}_{pp}(H^-) = -1.08$ eV, we find $k = 0.7593$ and from Eq. (26) we obtain $E_{\mathrm{corr}} = -4.08$ eV. This value is inbetween the two limiting estimates which we just stated. It appears to be a good value.

Conclusion

The comparison of the present results with those given by other methods shows that a simple semi-empirical model based on Sinanoğlu's many electron theory for singlet ground states (MET) is adequate to approximately predict the correlation energies of the π-electron systems. The present form of the effective pair correlation energy method (F2-Approximation) can be applied to any singlet, single determinantal system in which every atom contributes only one electron to the molecular orbitals. The extension of the method to all systems including σ electrons requires further and quite different approximations which can be made on the LCAO form of the MET pair correlations derived recently [8]. A number of semi-empirical methods for E_{corr} of σ molecules are derived in subsequent papers by Sinanoğlu and by Pamuk.

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$$E_{\text{corr}} = E^{\pi}_{\text{corr}} + E^{\sigma}_{\text{corr}} + E^{\sigma\pi}_{\text{corr}} .$$

Further $\sigma - \pi$ interactions are predicted to be appreciable [5b, 9]. The theory also shows that -correlations change with the occupation of π-MO's (MET-"exclusion effect"). For σ, π-electron spectra, the non-closed shell theory (NCMET) [4] provides a rigorous and practicable theoretical framework. Progress along these lines has been made recently by K. Freed (to be published) and W. Rienhardt (to be published).

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22. Pamuk [17] initially arrived at Eq. (11) in somewhat more *ad hoc* ways than presented in this paper. That, Eq. (10) yields Eq. (11) when substituted in Sinanoğlu's equation (4) has been noticed more recently by the present authors.

23. Prior to the appearance of the first theoretically reasonable value of $E(2p_z^2)$ in the literature given by McKoy and O. Sinanoğlu (Ref. [5b]; "MET V") based on MET, it had been customary to neglect, e.g. in the L-shell of Neon atom, all $2s2p$ and other correlations except $(2p^2)$ $(i = x, y, z)$. This neglect led to very large (3 eV) values of $E(2p_z^2)$.

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