

Semi-Empirical Effective Pair Correlation Parameters and Correlation Energies of BH, CH, NH, OH, HF, N₂, and CH₄

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A set of approximations ("EPCE-F2 σ ") is given for estimating the correlation energies of molecules. The approximations start from Sinanoğlu's pair correlations and his many-electron theory for ground states (MET). For application of this method, "effective pair correlation energies" must be known. In the present paper three sets of one-center effective pair correlation energies are obtained from the atomic pair correlation energies. A weighted average method is introduced for handling the non-transferable atomic correlation energies. For the corresponding two-center effective pair correlation energies several empirical expressions are given. Then using three sets of one-center effective pair correlation energies and for the two-center ones, the correlation energies of some diatomic hydrides, N₂ and CH₄ molecules are estimated. The results agree quite well with each other, with experimental values, and with those obtained by other methods.

Ein Näherungsverfahren („EPCE-F2 σ “) zur Abschätzung der Korrelationsenergie von Molekülen wird angegeben. Die Näherungen gehen von Sinanoglus Paarkorrelation und seiner Mehrelektronentheorie für Grundzustände (MET) aus. Zur Anwendung dieser Methode müssen „Effektive Paarkorrelationsenergien“ bekannt sein. In der vorliegenden Veröffentlichung werden drei Sätze von solchen effektiven Paarkorrelationsenergien für ein Zentrum aus atomaren Paarkorrelationsenergien gewonnen. Zur Behandlung der nichtübertragbaren atomaren Korrelationsenergien wird eine Methode mit gewichteten Mittelwerten angewendet. Für die entsprechenden effektiven Paarkorrelationsenergien für zwei Zentren werden verschiedene semiempirische Ausdrücke angegeben. Mit je drei Sätzen von Werten für die genannten Energiewerte für ein Zentrum oder zwei Zentren werden die Korrelationsenergien für einige zweiatomige Hydride sowie die Moleküle N₂ und CH₄ abgeschätzt. Die Ergebnisse stimmen gut untereinander und mit experimentellen Werten sowie mit Werten aus anderen Verfahren überein.

Introduction

In a previous paper [1], Sinanoğlu and Pamuk have given a semi-empirical one and two center effective pair correlation method for estimating the correlation energies of π -electron systems. This method applied to planar π -systems, each center contributing one $2p\pi$ -orbital or similarly to systems like a cluster of Hydrogen atoms with an s -orbital for each center. The method is based on Sinanoğlu's "Many-Electron Theory of Atoms and Molecules" (MET) for ground states and the breakdown of total correlation energy of such systems into $N(N-1)/2$, MO pair correlations introduced by him [2]. For doubly occupied ground states, Sinanoğlu has recently derived a LCAO-MET form of the theory, and from it a number of semi-empirical molecular correlation approximations. In the π -system paper [1], a more approximate form of these methods which applied strictly to π -systems on account of symmetry was used and was referred to as the MET-

EPCE-F2 method (EPCE = effective pair correlation energy) with the equation.

$$E_{\text{corr}}^{\pi} \underset{\text{(F2)}}{\cong} \frac{1}{4} \sum_{p,q} P_{pp} P_{qq}^* \bar{\varepsilon}_{pq} \quad (1a)$$

where $P_{pq} = 2 \sum_k c_p^k c_q^{k*}$, the charge and bond order matrix and

$$\bar{\varepsilon}_{pq} \equiv \varepsilon_{p^{\alpha}q^{\beta}} + \varepsilon_{p^{\alpha}q^{\alpha}} \quad (1b)$$

referred to as (EPC). The ‘‘F2-approximation’’ involved the assumption

$$\varepsilon_{p^{\alpha}q^{\beta}} \cong 2\varepsilon_{p^{\alpha}q^{\alpha}} \quad (1c)$$

which led to the vanishing of the P_{pq} ($p \neq q$) terms from Eq. (1a). The latter terms had not been noticed earlier and omitted as such by independent users of Eq. (1a) by Pamuk [4] and by Brown and Roby [5]. The $(\varepsilon_{pp}, \varepsilon_{pq})$ -method had first been suggested by Sinanoğlu [6] by approximations analogous to ZDO on the MET equations, but without the further approximation, Eq. (1c).

In the present paper, we use the MET-EPCE-F2-method for non- π -molecules including $2s$, $2p_{x,y,z}$ orbitals, although this use implies many more approximations for sigma systems than the original π -case. These additional assumptions are discussed below. The use of an analog of Eq. (1a) for various molecules like diatomics, CH_4 , etc. is not as rigorous as Sinanoğlu’s new semi-empirical MO-MET-methods [3], nevertheless with the $\bar{\varepsilon}_{pq}$ -average parameters evaluated and given in this paper, the results on total E_{corr} ’s of many molecules are quite good.

The Use of MET-EPCE-F2 Method for Sigma Molecules

The approximations that lead to Eq. (1a) are not invariant under atomic coordinate transformations in non- π systems. Further in a general molecule of first row atoms with $2s$, $2p$ valence electrons there will be ‘‘cross pair correlations’’ as shown by the Sinanoğlu Non-Closed Shell correlation theory [2b]. In spite of these additional complexities we may use Eq. (1a) for sigma systems too in a more *ad hoc* way, assuming 1) the sum of all cross pairs are small or vanish, 2) the F2-approximation, Eq. (1c) is reasonable (certainly more than the full ZDO-like one of $\varepsilon^{\alpha\beta} \approx \varepsilon^{\alpha\alpha}$) in the P_{pq} ($p \neq q$) only, 3) that the approximations hold in a given set of atomic coordinate frames only, as in the Brown-Roby approach [5], as contrasted by Pople’s, to approximate MO-theory, and 4) that when actual MO’s with non-zero overlaps are available, the P_{pp} ’s of π -theory in Eq. (1a) become replaced by Mulliken *gross populations* [7], Q_{pA} .

The last assumption is somewhat justified [4] if one uses the Mulliken Approximation (MULAP) for overlap charges, or if MO’s can be expanded in a series in overlap integrals $S_{p_A q_B}$, although neither approximation is particularly effective in other than π -orbitals. With the usual gross populations we have for Eq. (1a),

$$E_{\text{corr}} \underset{\text{F2}\sigma}{\cong} \sum_{A,B} \sum_{p,q} \left(\sum_k \frac{Q_{pA}^k}{N_k} \right) \left(\sum_l \frac{Q_{qB}^l}{N_l} \right) \bar{\varepsilon}_{p_A q_B} \quad (1d)$$

where k, l are spinless MO’s, and $N_k = N_l = 2$ for doubly occupied ground states.

To emphasize that the present method on σ -systems involves quite different approximations than the use of Eq. (1a) for π -systems, we shall refer to it, i.e. Eq. (1b) as the "EPCE-F2 σ -method". We shall test the validity of the $\varepsilon_{\mu\mu}$, $\bar{\varepsilon}_{\mu\nu}$, AO-correlation parameters obtained below with application to diatomic hydrides as well as N₂ and CH₄.

Atomic Correlation Energies and their Use as One-Center Effective Pair Correlation Energies

In the theory of electron correlation in non-closed shells, i.e. Sinanoğlu's NCMET correlation energy is rigorously separated into three parts [2b]. (i) Internal correlation energy; (ii) Semi-internal correlation energy; (iii) All-external correlation energy. The corresponding correlations can be interpreted as virtual electrons come close to each other, they will interact and be virtually excited to other orbitals. The internal correlation energy is due to excitations within the H.F. (Hartree-Fock) sea. The semi-internal correlation energy is due to excitations in which an electron is excited to outside the H.F. sea and a second one is excited to a previously unoccupied one in the H.F. sea. The all external correlation energy is due to excitations to outside the H.F. sea. This is the only type which can occur in closed shell systems like Ne atom.

Because of the exclusion effect and the dependence of the pair correlation energies on the total H.F. potential, the internal and semi-internal correlation energies are strongly dependent on the total orbital angular momentum, L , total spin, S , the number of $2p$ electrons, and the charge of the nucleus, Z . (These are called environmental effects). The all-external Sinanoğlu pair correlation energies are independent of the overall L , and S values. These can be transferred from the atoms to their ions and vice-versa. They are only slightly dependent on Z . If we find the contribution of each pair to the internal and semi-internal correlation energies, then the atomic pair correlation energies can be expressed in two parts: a) Dynamical or transferable part which comes from the all external correlation energy; and b) Nondynamical or nontransferable part which comes from the internal and semi-internal correlation energies [8–12].

The (1s) electron-pair of atoms in molecules are not very different from those of free atoms. It can be assumed that the atoms in molecules contain two 1s electrons. But the number of the electrons on the other orbitals are rather different from those of free atoms. In general, the electron configuration of a first row atom in molecules can be taken as $1s^2 2s^n 2p^m$ where $0 \leq n \leq 2$ and $0 \leq m \leq 6$. This configuration does not correspond to a certain spectroscopic state but it can be approximated by taking a linear combination of several spectroscopic states [13]. Therefore, one center effective pair energies have to be found by taking the average values of the corresponding pair correlation energies of these states. However, the total correlation energy of a molecule is expressed in the (EPCE-F2 σ)-method by Eq. (1d), where $Q_{p_A}^k$ is the partial gross atomic population on p^{th} AO of the A^{'th} atom in the k^{th} MO; N_k is the number of the electrons in the k^{th} MO, and $\bar{\varepsilon}_{p_A q_B}$ is the effective pair correlation energy between the electrons on p^{th} AO of atom A and q^{th} AO of atom B. (The effective pair correlation energies are the sum of ($\alpha\alpha$) and ($\alpha\beta$) pair energies, Eq. (1b)). As we see in Eq. (1), the contribution of an effective

pair correlation energy to the total correlation energy, is not its own value but the product

$$\left[\sum_k (Q_{p_A}^k / N_k) \right] \left[\sum_l (Q_{d_B}^l / N_l) \right] \bar{\epsilon}_{p_A q_B}. \quad (2)$$

Hence, the electron populations partially take care of the electron promotion from the $2s$ orbital to $2p$ orbitals. Therefore, it seems that it is enough to take the average values of the pair energies coming from the spectroscopic states of $1s^2 2s^2 2p^n$ ($n = 0, \dots, 6$) configurations.

For the above configurations the internal and semi-internal correlation energies are contributed by $2s \leftrightarrow 2s$ and $2s^2 \leftrightarrow 2p^n$ correlations, respectively. Thus, for a certain spectroscopic state, we may assume that (i) with the exception of $\bar{\epsilon}_{2s^2}$ and $\bar{\epsilon}_{2s 2p}$, the nontransferable parts of all pair correlation energies are negligible; (ii) the internal correlation energy can be taken as the nontransferable part of the $\bar{\epsilon}_{2s^2}$ effective pair correlation energy, (iii) the semi-internal correlation energy divided by the number of the $2p$ electrons can be taken as the nontransferable part of the $\bar{\epsilon}_{2s 2p}$ effective pair energies.

Since the transferable parts of the pair correlation energies are the same for all spectroscopic states of a certain atom, we do not need to find their average values. The average of the nontransferable parts can be found by giving appropriate weighting for multiplicity of the states coming from the ground state configurations $1s^2 2s^2 2p^n$ (for each n).

$$\bar{\epsilon}_{p_A q_A}(\text{ntr}) = \frac{\sum_i (2L_i + 1)(2S_i + 1) \bar{\epsilon}_{p_A q_A}^i(\text{ntr})}{\sum_i (2L_i + 1)(2S_i + 1)} \quad (3)$$

where $\bar{\epsilon}_{p_A q_A}(\text{ntr})$ is the average nontransferable part of the effective pair correlation energy $\bar{\epsilon}_{p_A q_A}$ which is dependent on the number of $2p$ electrons; $\bar{\epsilon}_{p_A q_A}^i(\text{ntr})$ is the nontransferable part of the $\bar{\epsilon}_{p_A q_A}$ in the i 'th spectroscopic state; L_i and S_i are the total orbital angular momentum and the total spin of the same spectroscopic state; summations are taken over all states coming from the configuration $1s^2 2s^2 2p^n$. Finally we can assume that the nontransferable parts of $\bar{\epsilon}_{2s^2}$ and $\bar{\epsilon}_{2s 2p}$ pair correlation energies change continuously and smoothly with the number of $2p$ electrons, n , of the atom in molecules. Hence we fit the polynomials

$$\bar{\epsilon}_{2s^2}(\text{ntr}) = an^2 + bn + c \quad (4)$$

and

$$\bar{\epsilon}_{2s 2p}(\text{ntr}) = dn^2 + en + f. \quad (5)$$

The coefficients of these polynomials will be found in the next section. Eq. (5) is not applicable if $n \cong 0$.

One-Center Effective Pair Energies

Several approximations are involved in the determination of the two-center and nontransferable part of the one-center effective pair correlation energies. Therefore, the best atomic pair correlation energies may not give the best molecular correlation energies. This must be checked by numerical calculations. Con-

sequently, it is better to try several sets of one-center effective pair correlation energies and choose the set which yields the value closest to the experimental correlation energies. Here, the experimental correlation energy of a molecule is defined as

$$E_{\text{corr}}^{\text{exp}} \equiv BE_{\text{H.F.}} - BE_{\text{exp}} + \sum_{\text{atoms}} E_{\text{corr}}(\text{atoms}) \quad (6)$$

where relativistic correction is neglected.

Set A. The transferable one-center effective pair correlation energies are listed in Table 1. The values of the $\bar{\epsilon}_{1s^2}(\text{tr})$ and $\bar{\epsilon}_{1s2s}(\text{tr})$ are from Ref. [15]. The transferable part of the $\bar{\epsilon}_{2s^2}$ pair correlation energies are obtained from the dynamical $\bar{\epsilon}_{2s^2}$ values for (N, ^4S) and (Ne, ^1S) which are from Ref. [8b]. It is assumed that they change linearly with the nuclear charge. The $\bar{\epsilon}_{2s2p}(\text{tr})$, $\bar{\epsilon}_{2p_x2p_y}(\text{tr})$ and $\bar{\epsilon}_{2p_z^2}(\text{tr})$ for C, N, and O atoms are from Ref. [10a]; those for B and F atoms are found by extrapolation and may be less accurate than the other pair correlation energies.

The nontransferable parts of the $\bar{\epsilon}_{2s^2}$ and $\bar{\epsilon}_{2s2p}$ pair correlation energies are tabulated in Tables 2 and 3, respectively. They are determined as described in the

Table 1. Transferable one-center effective pair correlation energies in set A (in eV)

| Pairs | B | C | N | O | F |
|-----------------------------|--------|--------|--------|--------|--------|
| $\bar{\epsilon}_{1s^2}$ | -1.219 | -1.227 | -1.233 | -1.238 | -1.241 |
| $\bar{\epsilon}_{1s2s}$ | -0.112 | -0.138 | -0.156 | -0.190 | -0.220 |
| $\bar{\epsilon}_{1s2p}$ | -0.1 | -0.1 | -0.1 | -0.1 | -0.1 |
| $\bar{\epsilon}_{2s^2}$ | -0.03 | -0.107 | -0.166 | -0.210 | -0.244 |
| $\bar{\epsilon}_{2s2p}$ | -0.30 | -0.35 | -0.41 | -0.46 | -0.52 |
| $\bar{\epsilon}_{2p_x2p_y}$ | -0.98 | -0.81 | -0.63 | -0.52 | -0.46 |
| $\bar{\epsilon}_{2p_z^2}$ | -1.11 | -1.04 | -0.97 | -0.92 | -0.90 |

^a See text; note that $\bar{\epsilon}_{pq} \equiv (\epsilon_{p\alpha q\beta} + \epsilon_{p\alpha q\alpha})$.

Table 2. Average $\bar{\epsilon}_{2s^2}(\text{ntr})$ correlation energies^a in set A

| <i>n</i> | 0 ^b | 1 | 2 | 3 | 4 |
|----------|----------------|--------|---------|--------|--------|
| B | -1.417 | -0.811 | (-0.43) | — | — |
| C | -1.828 | -1.109 | -0.524 | -0.177 | — |
| N | -2.309 | -1.329 | -0.659 | -0.273 | -0.066 |
| O | -2.554 | -1.541 | -0.775 | -0.336 | -0.090 |

^a In electron volts; ($\bar{\epsilon} \equiv \epsilon(\alpha\beta) + \epsilon(\alpha\alpha)$).

^b *n* = 0 values are from Ref. [8].

Table 3. Average $\bar{\epsilon}_{2s2p}(\text{ntr})$ correlation energies^a in set A

| <i>n</i> | 1 | 2 | 3 | 4 | 5 |
|----------|---------|---------|---------|---------|---------|
| B | -0.647 | (-0.44) | — | — | — |
| C | -0.760 | -0.486 | -0.272 | — | — |
| N | -0.790 | -0.541 | -0.356 | -0.183 | -0.064 |
| O | -0.800 | -0.578 | -0.393 | -0.223 | -0.100 |
| F | (-0.81) | (-0.60) | (-0.42) | (-0.27) | (-0.13) |

^a In electron volts ($\bar{\epsilon} \equiv \epsilon(\alpha\beta) + \epsilon(\alpha\alpha)$).

Table 4. Coefficients for the polynomials in Eqs. (4) and (5) for set *A*

| Atom | a | b | c | d | e | f |
|------|--------|-------|--------|--------|-------|--------|
| B | -0.113 | 0.719 | -1.417 | 0.0 | 0.207 | -0.854 |
| C | -0.119 | 0.942 | -1.932 | -0.030 | 0.364 | -1.094 |
| N | -0.090 | 0.836 | -1.971 | -0.018 | 0.275 | -1.019 |
| O | -0.097 | 0.924 | -2.235 | -0.017 | 0.273 | -1.056 |
| F | — | — | — | -0.005 | 0.185 | -0.930 |

Table 5. Transferable one-center effective pair correlation Energies^a in set *B*

| Pairs | B | C | N | O | F |
|---------------------------------|----------|--------|--------|--------|--------|
| $\bar{\varepsilon}_{1s^2}$ | -1.221 | -1.240 | -1.256 | -1.261 | -1.266 |
| $\bar{\varepsilon}_{1s2s}$ | -0.104 | -0.090 | -0.071 | -0.082 | -0.079 |
| $\bar{\varepsilon}_{1s2p}$ | -0.102 | -0.102 | -0.102 | -0.102 | -0.102 |
| $\bar{\varepsilon}_{2s^2}$ | -0.060 | -0.102 | -0.147 | -0.190 | -0.230 |
| $\bar{\varepsilon}_{2s2p}$ | -0.421 | -0.407 | -0.420 | -0.431 | -0.446 |
| $\bar{\varepsilon}_{2p_x 2p_y}$ | (-0.766) | -0.719 | -0.661 | -0.607 | -0.572 |
| $\bar{\varepsilon}_{2p_z^2}$ | (-0.730) | -0.763 | -0.781 | -0.741 | -0.729 |

^a In electron volts. $\bar{\varepsilon}_{pq} \equiv \varepsilon_p \alpha_q \beta + \varepsilon_p \alpha_q \alpha$

Table 6. Average $\bar{\varepsilon}_{2s} 2(\text{ntr})$ correlation energies^a in set *B*

| <i>n</i> | 0 ^b | 1 | 2 | 3 | 4 |
|----------|----------------|--------|--------|--------|--------|
| B | -1.417 | -0.802 | -0.292 | — | — |
| C | -1.828 | -1.088 | -0.533 | -0.187 | — |
| N | -2.309 | -1.313 | -0.679 | -0.286 | -0.073 |
| O | -2.554 | -1.522 | -0.801 | -0.352 | -0.100 |

^a In electron volts. $\bar{\varepsilon} \equiv \varepsilon(\alpha\beta) + \varepsilon(\alpha\alpha)$.

^b *n* = 0 values are taken from Ref. [8].

Table 7. Average $\bar{\varepsilon}_{2s 2p}(\text{ntr})$ correlation energies^a in set *B*

| <i>n</i> | 1 | 2 | 3 | 4 | 5 |
|----------|--------|--------|--------|--------|--------|
| B | -0.586 | -0.368 | — | — | — |
| C | -0.662 | -0.481 | -0.299 | — | — |
| N | -0.714 | -0.535 | -0.364 | -0.202 | — |
| O | -0.747 | -0.568 | -0.398 | -0.247 | -0.110 |
| F | -0.771 | -0.589 | -0.421 | -0.255 | -0.125 |

^a In electron volts $\bar{\varepsilon} \equiv \varepsilon(\alpha\beta) + \varepsilon(\alpha\alpha)$.

Table 8. Coefficients for the polynomials in Eqs. (4) and (5) for set *B*

| Atom | a | b | c | d | e | f |
|------|--------|-------|--------|--------|-------|--------|
| B | -0.053 | 0.668 | -1.417 | 0.0 | 0.218 | -0.804 |
| C | -0.100 | 0.847 | -1.828 | 0.0 | 0.181 | -0.843 |
| N | -0.090 | 0.843 | -2.005 | -0.005 | 0.196 | -0.906 |
| O | -0.099 | 0.944 | -2.293 | -0.007 | 0.200 | -0.935 |
| F | — | — | — | -0.018 | 0.292 | -1.135 |

previous section using the internal and semi-internal correlation energies for C, N, and O atoms given by Skutnik [10a] and by McKoy and Sinanoğlu [8b]. The values in parentheses are obtained by extrapolation.

Table 4 contains the coefficients for the polynomials in Eqs. (4), (5). The internal correlation energy is zero if there are 5 or more $2p$ electrons, because all space orbitals in the HF seas are occupied. The $2p$ population of the F atom in molecules is usually greater than 5. Therefore, the nontransferable parts of $\bar{\epsilon}_{2s^2}$ pair energies for the F atom and its ions are not listed.

Set B. Recently Öksüz and Sinanoğlu have developed computer programs to obtain the internal and the semi-internal correlation energies of all states of the first row atoms and their ions [11], based on Sinanoğlu's Non-closed shell electron correlation and atomic structure theory [2b]. The experimental all-external energies are found from these values and from the experimental total correlation energies. The above workers have carried out two sets of least square analyses. In the first set they used the experimental all-external correlation energies for only the ground configuration $1s^2 2s^2 2p^n$ ($n = 1 - 6$). In the second set, they included all states coming from the $1s^2 2s 2p^2$ and $1s^2 2s 2p^3$ as well as the ground configurations. In Table 5 the transferable pair energies obtained from the ground configurations alone are listed. The $\bar{\epsilon}(2p_x 2p_y)$ and $\bar{\epsilon}(2p_z^2)$ effective pair energies for the B atom are obtained by extrapolation.

The nontransferable parts of the $\bar{\epsilon}_{2s^2}$ and the $\bar{\epsilon}_{2s 2p}$ are obtained from Eq. (3) using the internal and the semi-internal correlation energies which are from Refs. [8, 10b, 11]. They are tabulated in Tables 6 and 7. The coefficients of the polynomials in Eqs. (4), (5) are determined from these values and listed in Table 8.

Set C. The $\bar{\epsilon}(2p_x^2)$ effective pair correlation energy in Set B is much smaller than the empirically found one-center or two-center effective pair correlation energies for the π -electron systems. This is due to the neglect of the non-transferable part of $\bar{\epsilon}(2p_x^2)$ effective pair energy. The study of the one and two-center correlation energies for the Hydrogen molecule [14] and for π -electrons [1] has shown that the one-center pair correlation energies are slightly larger than the two-center effective pair energies at the equilibrium. Therefore, in this set, we disregard the calculated values of the $\bar{\epsilon}(2p_x^2)$ atomic pair correlation energy of the carbon atom. Using only the $\bar{\epsilon}(2p_x^2)$ pair energies for the N, O, and F atoms in the Set B we fit an equation:

$$\bar{\epsilon}_{(2p_x^2)}^A = -0.014Z_A^2 + 0.250Z_A - 1.845 \text{ (e.V.)} \quad (7)$$

where Z_A is the nuclear charge of the atom A. Eq. (7) yields $\bar{\epsilon}_{(2p_x^2)}(C) = -0.849$ eV and $\bar{\epsilon}_{(2p_x^2)}(B) = -0.945$ eV. Other one-center effective pair energies in this set are the same as in Set B.

Two-Center Effective Pair Correlation Energies

Previously [1], for larger distances than the equilibrium bond length, we have assumed that the two-center effective pair energies can be represented by

$$\bar{\epsilon}_{p_A q_B} = 0.5(\bar{\epsilon}_{p_A p_A} + \bar{\epsilon}_{q_B q_B}) f(R_{AB}, p_A, q_B). \quad (8)$$

where $\bar{\epsilon}_{p_A p_A}$ and $\bar{\epsilon}_{q_B q_B}$ are one-center pair correlation energies; $f(R_{AB}, p_A, q_B)$ is a function of the internuclear distance and the orbital exponents of the AO's p_A and q_B . Unfortunately, we do not have an exact expression for the function f . Therefore, we shall use empirical functions which can represent the ratio of the two-center effective pair correlation energy to the sum of the one-center effective pair energies for the H_2 molecule up to the $2R_e$ with an error less than ± 0.05 eV. Thus we define the new function $F_{p_A q_B}$ as

$$F_{p_A q_B} = \bar{\epsilon}_{p_A q_B} / (\bar{\epsilon}_{p_A p_A} + \bar{\epsilon}_{q_B q_B}). \quad (9)$$

Fischer-Hjalmar's gives the following relation between $F_{p_A q_B}$ and $F_{r_{CS_D}}$ [14]:

$$F_{p_A q_B} = k[S_{p_A q_B}^2 / S_{r_{CS_D}}^2] F_{r_{CS_D}}, \quad (10)$$

where $S_{p_A q_B}$ and $S_{r_{CS_D}}$ overlap integrals and k is a scaling parameter. We found that $F_{p_A q_B}$ can be represented by

$$F_{p_A q_B}^{(1)} = (k_1 R_{AB} + 0.1) S_{p_A q_B}^2. \quad (11)$$

Since we shall introduce other approximate expressions, to indicate that this is the first approximation, we use (1) as a superscript. The two-center pair energies for the H_2 molecule taken from Ref. [14] and k_1 scaling parameters obtained from Eqs. (9) and (11) are listed in the third and the fourth columns of Table 9. The scaling parameter k_1 is approximately constant for distances smaller than 3 a.u.

Coulson has studied the change of the exponent of the H_2 molecule with the internuclear distance [16]. In Ref. [16] the exponents are given for internuclear distances different from those given in Table 9. The exponents given in this table are obtained by extrapolation. Of course, overlap integrals, $S_{p_A q_B}$, have different values if these exponents are used instead of the atomic value $\zeta = 1$. Now the following expression is found to represent $F_{p_A q_B}$:

$$F_{p_A q_B}^{(2)} = (k_2 \varrho_{p_A q_B} - 0.08) S_{p_A q_B}^2 \quad (12)$$

where

$$\varrho_{p_A q_B} = 0.5(\zeta_{p_A} + \zeta_{q_B}) R_{AB}. \quad (13)$$

The scaling parameter k_2 , given in the fifth column of Table 9, is also approximately constant up to $2R_e = 2.8$ a.u. If $k_1 = 0.5$ and $k_2 = 0.63$ are chosen as the best

Table 9. Two-center correlation energies for the H_2 molecule and parameters for approximate $F_{p_A q_B}$'s

| R_{AB} (a.u.) | ζ^a | ϵ_{pq}^b (eV) | k_1 | k_2 | k_3 | k_4 |
|-----------------|-----------|------------------------|-------|-------|-------|-------|
| 1.2 | 1.240 | -0.979 | 0.496 | 0.631 | 12.68 | 10.66 |
| 1.4 | 1.185 | -0.964 | 0.491 | 0.631 | 12.81 | 10.44 |
| 1.6 | 1.140 | -0.930 | 0.491 | 0.632 | 12.69 | 10.48 |
| 1.8 | 1.105 | -0.880 | 0.494 | 0.632 | 12.96 | 10.61 |
| 2.0 | 1.075 | -0.817 | 0.500 | 0.628 | 12.55 | 10.86 |
| 2.2 | 1.050 | -0.741 | 0.503 | 0.619 | 12.27 | 10.63 |
| 2.6 | 1.005 | -0.573 | 0.501 | 0.579 | 11.78 | 10.66 |
| 3.0 | 1.0 | -0.397 | 0.471 | 0.535 | 10.91 | 10.91 |
| 3.5 | 1.0 | -0.198 | 0.361 | 0.415 | 8.47 | 8.47 |
| 4.0 | 1.0 | -0.035 | 0.090 | 0.137 | 2.53 | 2.53 |

^a From Ref. [16]. — ^b From Ref. [14].

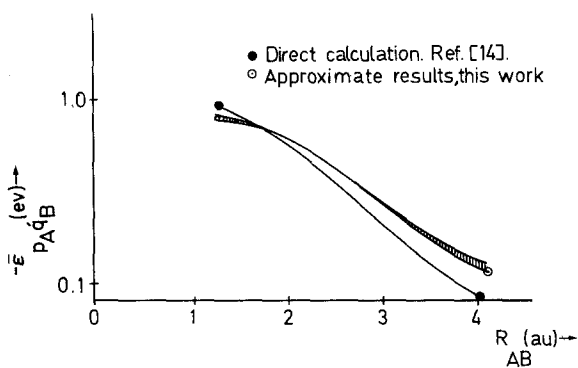


Fig. 1. Two-center correlation energy for the H_2 molecule

scaling parameters, naturally at large distances, the $\bar{\epsilon}_{p_A q_B}$ effective pair energies obtained by these approximate expressions will be larger than the ones given in Table 9. However, the values of $\bar{\epsilon}_{p_A q_B}$ effective pair energies at large distances are small and may be less accurate.

When these expressions are generalized to all two-center effective pair energies, Eq. (10) is automatically satisfied if 0.1 in Eq. (11) and 0.08 in Eq. (12) are neglected. However, Eqs. (11) and (12) predict $\bar{\epsilon}_{p_A q_B} = 0$ if p_A and q_B are orthogonal orbitals. The correlation energy of electrons on such orbitals may be small but it is not necessarily zero. The use of charge overlap integrals

$$C_{p_A q_B} \equiv \langle \chi_{p_A}^2, \chi_{q_B}^2 \rangle \quad (14)$$

may give better results, where χ_p and χ_q are atomic orbitals. Therefore, we assume two more expressions for $F_{p_A q_B}$

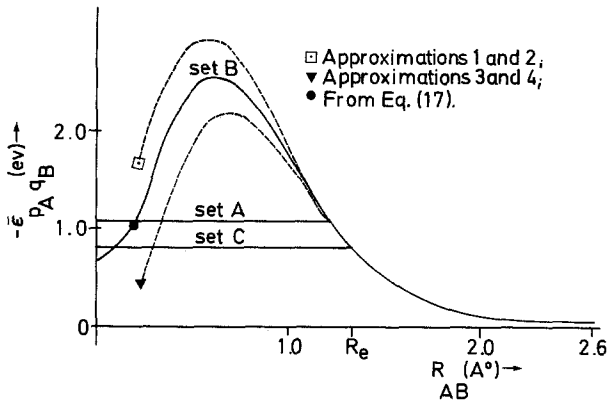
$$F_{p_A q_B}^{(3)} = k_3 C_{p_A q_B} R_{AB}^2 \quad (15)$$

and

$$F_{p_A q_B}^{(4)} = k_4 C_{p_A q_B} e_{p_A q_B}^2. \quad (16)$$

For the H_2 molecule k_3 and k_4 scaling parameters are calculated and listed in the last two columns of Table 9. The use of $k_3 = 12.5$ and $k_4 = 10.4$ yields also high values for $\bar{\epsilon}_{p_A q_B}$ at large distances. The pair correlation energies obtained by these approximations are plotted versus internuclear distance in Fig. 1.

The best approach would be to determine as few parameters as possible. However, we have chosen three sets of one-center effective pair correlation energies and we have to determine three sets of corresponding two-center ones. If the internuclear axis is taken as the X -axis, we will denote an electron on the H atom by h , an electron on any first row atom by a , an electron on the $2p_y$ or on the $2p_z$ orbitals of the first row atoms by π , and an electron on other orbitals of the first row atoms by σ . The preliminary applications of the EPCE method have indicated that for each approximation of the two-center pair correlation energies we have to determine different scaling parameters at least for four types of pairs in order to obtain the correlation energies of N_2 and CH_4 comparable to the experimental values. These are $h-h$, $\pi-\pi$, $h-a$ and $\sigma-a$ type pairs. The parameters for $h-h$ type pairs have already been determined.

Fig. 2. Two-center correlation energy for $\pi - \pi$ type pairsTable 10. Parameters for $F_{p_A q_A}$'s

| Type of pair | k_1 | k_2 | k_3 | k_4 | |
|--------------|------------|-------|-------|-------|-------|
| $h-h$ | 0.50 | 0.63 | 12.50 | 10.40 | |
| Set A | $h-a$ | 0.60 | 0.45 | 4.50 | 2.00 |
| | $\sigma-a$ | 0.90 | 0.45 | 2.10 | 0.55 |
| | $\pi-\pi$ | 2.34 | 1.49 | 23.60 | 8.93 |
| Set B | $h-a$ | 0.77 | 0.54 | 5.46 | 2.51 |
| | $\sigma-a$ | 1.15 | 0.54 | 2.62 | 0.49 |
| | $\pi-\pi$ | 3.55 | 2.26 | 31.78 | 12.03 |
| Set C | $h-a$ | 0.73 | 0.52 | 5.25 | 2.40 |
| | $\sigma-a$ | 1.13 | 0.58 | 3.20 | 0.84 |
| | $\pi-\pi$ | 2.87 | 1.86 | 29.41 | 11.14 |

The parameters for $\pi-\pi$ type pairs are determined from $\bar{\epsilon}_{pq} = -0.794$ eV (the two-center effective pair correlation energies for the π electrons at the bond length of the benzene molecule), and from the one-center effective pair correlation energies of $\bar{\epsilon}(2p_z^2)$ in each set. The necessary overlap and charge overlap integrals are calculated from the equations given in Appendices D and E of Ref. [17]. In the Sets A and C $F_{p_A q_B}$ is set equal to 0.5 for internuclear distances shorter than the distance where $F_{p_A q_B} \geq 0.5$. In the Set B, this condition is relaxed because the one-center effective pair energy, $\bar{\epsilon}_{(2p_z^2)} = -0.763$ eV, is smaller than the two-center one, $\bar{\epsilon}_{pq} = -0.794$ eV. The results for the $F_{p_A q_B}$'s are plotted in Fig. 2. The values of the scaling parameters are given in Table 10.

The parameters for $h-a$ type pairs are determined so that every approximation in each set will yield the value closest to the experimental correlation energy of the CH_4 molecule. The H.F. energy of CH_4 has been calculated by several workers [18–20]. The best value is $E_{\text{H.F.}} = -40.1983$ a.u. which yields the H.F. binding energy $BE_{\text{H.F.}} = 13.868$ eV [20]. The experimental binding energy of methane is $BE_{\text{H.F.}} = 18.175$ eV [21]. From Eq. (6) and $E_{\text{corr}}(^3P\text{C}) = -4.299$ eV [15], we find the experimental correlation energy for the CH_4 molecule $E_{\text{corr}}^{\text{exp}} = -8.61$ eV. The electron populations are obtained from the wave function

given by Pitzer [22]. The overlap and charge overlap integrals are computed using the equations given in Appendices D and E of Ref. [17]. The calculated parameters are listed in Table 10.

The parameters for the $\sigma - a$ type pairs are determined using the experimental correlation energy for the N_2 molecule. The H.F. energy of N_2 is $E_{H.F.} = -108.9956$ a.u. which yields the H.F. binding energy, $BE_{H.F.} = 5.27$ eV [23]. The experimental binding energy of the N_2 molecule is $BE_{exp} = 9.906$ eV [21]. Using $E_{corr}(^4S, N) = -5.115$ eV [15] and Eq. (6) we find $E_{corr}^{exp} = -14.87$ eV. Electron populations are from Ref. [24]. The overlap and the charge overlap integrals are again calculated using the equations in Appendices D and E of Ref. [17]. The resulting parameters are also listed in Table 10.

The trial calculations for small molecules have shown that any of the four approximations can predict the correlation energies of these molecules within the ± 0.5 eV range of the experimental values. However, the standard deviation is smallest if

$$F_{p_A q_B} = [3F_{p_A q_B}^{(1)} + F_{p_A q_B}^{(2)} + 3F_{p_A q_B}^{(3)} + F_{p_A q_B}^{(4)}] / 8 \quad (17)$$

is used for the determination of the two-center effective pair energies.

For $F_{p_A q_B}$, Brown and Roby [25] have suggested the following expression

$$F_{p_A q_B} = 0.5 / [k_1 S_{p_A q_B}^{-1} + 0.5k_2 (\epsilon_{p_A p_A} + \epsilon_{q_B q_B}) R_{p_A q_B}^6] \quad (18)$$

with the following values $k_1 = 0.734424$, $k_2 = -0.257505$ (\AA^{-6} (eV) $^{-1}$) and $\epsilon_{p_A p_A} = \epsilon_{q_B q_B} = 1.1430$ eV. Since the denominator in this expression becomes zero for $R_{p_A q_B} = 1.328$ \AA , Eq. (18) cannot be used to estimate the ratio, given in Eq. (9), for any internuclear distance.

Preliminary Applications of the EPCE-F 2 σ Method

We have calculated the correlation energies of some diatomic hydrides, N_2 and CH_4 molecules to find out whether the one and two-center effective pair correlation energies yield acceptable values. The results are tabulated in Table 11. Experimental correlation energies obtained from the expression given in Eq. (6) are not the exact correlation energies. They contain the errors coming from the neglect of the relativistic effects, from the determination of the experimental binding energy, and from the H.F. calculations. Set *A*, Set *B*, and Set *C* are the results obtained by the EPCE method by using the effective pair correlation energy sets *A*, *B*, and *C* respectively. In these calculations two-center effective pair correlation energies are obtained from the expressions given in Eqs. (9) and (17). The "shrunk core" (S-C) and the "pair population method" (PPM) results are from Ref. [26]. With the exceptions of H.F. [27a], CH_4 [27b], and N^2 [28], the separated-ion (SI) values are calculated by us using the total correlation energies of atoms and ions [15]. Others [29, 30] have also calculated correlation energies of diatomic molecules by using the SI method. However, they give curves rather than the numbers, which makes comparison of them with the results of the EPCE method impossible.

In general correlation energies for diatomic molecules obtained by the EPCE method are in good agreement with those predicted by other methods and ex-

Table 11. Correlation energies of some small molecules (in eV)

| Molecule | $E_{\text{corr}}^{\text{exp}}$ | This work | | | S-C ^d | PPM ^d | SI ^j | |
|------------------------------|--------------------------------|----------------------|---------|---------|------------------|------------------|-----------------|----------------------|
| | | Set A | Set B | Set C | | | | |
| BH ^a | $^1\Sigma^-$ | - 4.20 ^c | - 4.78 | - 4.81 | - 4.81 | - 4.86 | - 4.20 | - 4.34 |
| CH ^b | $^2\pi$ | - 5.48 ^c | - 5.67 | - 5.69 | - 5.69 | - 5.98 | - 5.51 | - 5.67 |
| NH ^b | $^3\Sigma^-$ | - 6.82 ^c | - 6.93 | - 6.97 | - 6.93 | - 7.02 | - 6.47 | - 6.99 |
| OH ^b | $^2\Pi$ | - 8.62 ^c | - 8.51 | - 8.38 | - 8.60 | - 8.81 | - 8.47 | - 8.79 |
| HF ^b | $^1\Sigma^-$ | - 10.56 ^c | - 10.56 | - 10.49 | - 10.12 | - 10.69 | - 10.37 | - 10.83 ^e |
| N ₂ ^a | $^1\Sigma_g^-$ | - 14.96 ^f | - 14.93 | - 15.02 | - 14.95 | - 13.44 | - 14.17 | - 15.19 ^g |
| CH ₄ ^h | | - 8.61 | - 8.60 | - 8.63 | - 8.64 | — | - 7.99 | - 9.28 ⁱ |

^a Wave functions are from Ref. [31].

^b Wave functions are from Ref. [32].

^c These values are from Ref. [29].

^d These correlation energies are obtained by using E_{corr} of Ref. [26] and the atomic correlation energies of Ref. [15]. SC = "Shrunk-Core" method; PPM = "Pair Populations Method" of Hollister and Sinanoğlu [26].

^e This value is from Ref. [27a].

^f These are obtained from $E_{\text{corr}}^{\text{exp}}$ given in Ref. [26] and the atomic correlation energies of Ref. [15].

^g This value is from Ref. [28].

^h Wave function is from Ref. [22].

ⁱ This value is from Ref. [27b].

^j Separated-Ions estimate by the writer.

perimental correlation energies. In the case of diatomic hydrides, the "shrunk core method" reduces to the united atom (UA) approach [33]. This approach overestimates the correlation energy of molecules. The SI value for the HF molecule is larger in absolute value than the S-C result. If the correlation energy of the F⁻ ion is obtained by extrapolation from the correlation energies of the 10-electron isoelectronic series, the resulting correlation energy in absolute value would be smaller than 10.69 eV, and not 10.83 eV as given in Ref. [27a]. The direct calculation of the correlation energy by the CI method gives -8.41 eV for the H.F. molecule, which is only 80% of the experimental correlation energy [34].

The agreement between the "EPCE-F2 σ " results and the other values indicates that the effective pair correlation energies found here, can be used for all molecules. Another test for the weighted average method may be the calculation of the contribution of the \bar{e}_{2s^2} pair correlation energy of nitrogen atom in the N₂ molecule to the total correlation energy. This is calculated directly by a 2 × 2 CI and found to be approximately -0.3 eV per atom [26]. A rough estimation of this contribution was made by the PPM of Hollister and Sinanoğlu [12, 26]. We have calculated the $\bar{e}_{(2s^2)}$ effective pair correlation energy for nitrogen atom in N₂ by using Eq. (4), the coefficients given in Table 4, and the electron populations given in Ref. [31]. The values of $\bar{e}_{(2s^2)}$ are -0.368 eV in Set A and -0.389 eV in Set B, and C. The contributions of these to the molecular correlation energy are -0.279 eV in Set A and -0.295 in Sets B and C. Since these values are practically same as the 2 × 2 CI result, we expect to obtain better estimations by this method also for other atoms in molecules.

Conclusion

To estimate the correlation energy of a molecule by the present effective pair correlation energy method, (EPCE-F2 σ), the effective pair correlations have to be known. While developing the method, it was assumed that these can be determined empirically. In this paper, three sets of effective pair correlation energies are given. The use of atomic pair correlation energies as one-center effective pair correlation energies is modified and the "Weighted Average" method is introduced. We expect that this method will help to obtain better correlation energies because its application, to the calculation of the contribution of pair correlation energy of the nitrogen atom in the N₂ molecule, yields comparable results with that obtained by 2 \times 2 CI method.

For two-center effective pair correlation energies, several empirical expressions are given. However, the preliminary applications have indicated that a simple linear combination of them yields the best results. Using the one-center effective pair correlation energies and the final expression for the two-center effective pair correlation energies, the correlation energies of some diatomic hydrides, N₂ and CH₄ molecules are estimated. The results agree quite well with the experimental values. Therefore, it is expected the EPCE-F2 σ method will predict even the correlation energies of large molecules (i.e. benzene, naphthalene etc.) with less than 10% error. The best of the three sets of effective pair correlation energies may be chosen after applying the (EPCE-F2 σ) method to larger numbers of molecules.

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