Theoret. chim. Acta (Berl.) 30, 177—190 (1973)

Correlation Effects in the Neutral and Ionized Ground States of Acetylene*

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Received August 21, 1972/February 26, 1973

Correlation energies were calculated by "Effective Pair Correlation Energy" (EPCE) and minimal basis set configuration interaction (CI) methods for pairs of electrons in the occupied molecular orbitals for the (π_u^4) neutral ground state, (π_u^3) ground state of the positive ion, and $(\pi_u^4 \pi_g)$ ground state of the hypothetical negative ion of acetylene.

The EPCE values allow detailed breakdown of the ionization potential and electron affinity (for the unstable negative ion). It is seen that the SCF values for the former can be modified by the EPCE values to give estimates close to the experimental quantity.

The EPCE values are compared against the pair-wise correlation energies obtained by minimal basis set CI and the percentages of the latter as compared to the former are interpreted by considering the form of the available excited configurations used in constructing the correlated functions. The MBSCI calculation accounts for only 20–30% of the EPCE correlation energy.

Key words: Pair correlation – Acetylene – Ionic States – Configuration interaction

1. Introduction

If an electron is added to or removed from a molecule, there is little doubt concerning the importance of the electron or hole to the stability of the molecule. To see how the energy of a molecule changes in detail upon electron loss or capture, it is necessary to analyze the effects of correlation and reorganization among all the electrons of the system. It is possible to estimate the correlation energy in the various shells of a molecule as well as the correlations between different shells (which may be as large as the intrashell energies) using recent work of two of the authors [1] in the theory of electron correlation [2–5].

Separate developments [6] have indicated the importance of σ and π reorganization effects in the SCF wavefunctions of π-electron systems. It is interesting to compare correlation and charge reorganization effects on the energetics of electron loss and capture.

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*Supported by National Science Foundation Grant 31496X.

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Such an analysis is carried out, in this paper, for the neutral ground state, (Σ_n) (π_u^4), the lowest energy positive ion (Σ_c) (π_u^3), and the lowest energy negative ion (Σ_a) $(\pi_u^4\,\pi_g)$ of acetylene. The Σ configuration has identical occupancy for each species; the subscripts indicate that the σ electrons reorganize. The correlation energy is obtained by the semiempirical effective pair correlation energy (EPCE) [4, 5] and *ab initio* minimal basis set configuration interaction methods. More sophisticated calculations using an extended basis set may substantially revise the results presented here for the *ab initio* calculations. This calculation, partially completed 5 years ago [7], is an initial attempt to explore the correlation contributions to ionized states of a simple unsaturated molecule by partitioning the correlation energy into Σ, π, and $\Sigma-\pi$ contributions. Recently accurate calculations on H_2O and H_2O^+ have been carried out by Meyer [8], and on the neutral ground state of acetylene by Moskowitz [8a]. An important goal of this paper is a critical comparison of the EPCE and CI methods.

2. Correlation Energies from the Effective Pair Correlation Energy Method

In the EPCE method, the total correlation energy of a molecule is approximately given by

$$E_{\mathrm{corr}} = \sum_{k=1}^{n} \sum_{l=1}^{m} \bar{\varepsilon}_{kl} \tag{1}$$

where n and m are the numbers of the molecular orbitals which are occupied by the electrons with α and β spins respectively; $\bar{\varepsilon}_{kl}$ is the effective *molecular* pair correlation energy which is the sum of the $\alpha-\beta$ and $\alpha-\alpha$ molecular pair correlation energies.

The effective molecular pair correlation energies, in turn, are given in terms of $\bar{\varepsilon}_{p_\mathrm{A} q_\mathrm{B}}$'s, the effective *atomic* pair correlation energies, N_k and N_l, the numbers of the electrons occupying the molecular orbitals k and l, $Q_{p\mathrm{A}}^k$ and $Q_{q\mathrm{B}}^l$, the partial gross atomic populations [9]:

$$\bar{\varepsilon}_{kl} = \sum_{\mathrm{A}} \sum_{\mathrm{B}} \sum_{p} \sum_{q} (Q_{p\mathrm{A}}^k/N_k)\,(Q_{q\mathrm{B}}^l/N_l)\,\bar{\varepsilon}_{p_\mathrm{A} q_\mathrm{B}}\,. \tag{2}$$

Summations over A and B are taken over atoms, and p and q are over atomic orbitals on each atom. Generally, a limited basis set containing H atom 1*s* orbitals and first row atom 1*s*, 2*s*, and 2*p* orbitals is used in EPCE calculations. The atomic EPCE terms used in these calculations are the set *C* of Ref. [5].

The total correlation energy of a molecule containing π electrons can be separated into three parts by properly summing over the molecular orbitals:

$$E_{\mathrm{corr}} = E_{\mathrm{corr}}^{\sigma} + E_{\mathrm{corr}}^{\sigma-\pi} + E_{\mathrm{corr}}^{\pi} \tag{3}$$

where $E_{\mathrm{corr}}^{\sigma}$, $E_{\mathrm{corr}}^{\sigma-\pi}$ and E_{corr}^{π} are the correlation energies coming from the σ electrons only, interactions between the σ and π electrons, and π electrons only, respectively.

In the nonclosed shell many electron theory of the atomic systems, the total correlation energy is separated into three parts [3]: (i) transferable all-external correlation energy, (ii) nontransferable semi-internal correlation energy, (iii) nontransferable internal energy[1]. Molecules frequently are closed shell states. Therefore molecular correlation energy is expected to be mainly transferable. However the states of atoms in molecules can only be represented by taking the linear combination of their valence states instead of the ground states. Thus, if the molecular correlation energy is obtained from atomic correlation energies, part of the former will consist of nontransferable portions of atomic correlation energy introduced by the need to consider open-shell valence states for the atoms. It was assumed that internal and semi-internal correlation energies may be attributed to $2s-2s$, and to $2s-2p$ pairs, respectively [5].

Effective molecular pair correlation energies are given in Table 1. From this table, correlation energies between an electron in one of the inner orbitals ($1\sigma_g$ or $1\sigma_u$) and an electron in any other orbital are small corresponding to physical intuition that the innermost molecular orbitals originating in the C 1*s* atomic orbitals do not interact significantly with the molecular orbitals for the valence electrons. The physical intuition that the valence molecular orbitals should have significant interorbital, as well, as *intra*-orbital correlation energies is also maintained.

The correlation energies among the molecular orbitals are collected into groups composed of σ and π electrons alone, and into terms involving both types in Table 2. All-external, semi-internal and internal parts of each term are also given in the same table. The σ term is largest as is to be expected from the number of the σ electrons. The $\sigma-\pi$ term is also sizeable. Upon increasing the number of π electrons, both π and $\sigma-\pi$ terms increase because of the increased π population, whereas the σ term decreases. The σ term decrease is apparently mainly due to the decrease in the internal and the semi-internal parts of the atomic correlation parameters arising from the decrease in $\bar{\varepsilon}^2_{2s}$ and $\bar{\varepsilon}_{2s2p}$ with the increasing population of $2p$ electrons [5]. The π term contains only all-external parts because of the beginning hypothesis in obtaining the effective pair correlation energies. The partitioning of the all-external correlation energies may be realistic, but that of the nontransferable parts is subject to question. However these parts are usually less than 15% of the total correlation energy.

A breakdown of the terms entering the energetics of vertical ionization or vertical electron capture is given in Table 3. The terms are defined in Fig. 1 and in the subsequent paragraph. The ionization energy is given by

$$\Delta E\,(\text{total})^{n\to c} = \Delta E\,(K)^{n\to c} + \Delta E\,(\text{reorg})^{n\to c} + \Delta E\,(\text{corr})^{n\to c} + \Delta^2 E\,(\text{SCF})^{n\to c}. \tag{4}$$

The first term in Eq. (4) is the "approximate" Koopmans' Theorem [10] ionization energy where neither correlation nor reorganization effects are taken

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[1] "Internal correlation" is the term applied to the portion of the correlation which is described by configurations constructed by exciting two electrons from occupied orbitals to unoccupied orbitals while still remaining within the Hartree-Fock manifold of orbitals. "Semi-internal correlation" is described by configurations constructed by placing one excited electron in an orbital within the Hartree-Fock manifold and the other in an orbital outside the manifold (e.g. a 3*s* orbital for a first row atom). "External correlation" is described by configurations constructed by placing both excited electrons into orbitals outside the manifold. Transferable means that the value of the correlation energy is the same for different states of a given configuration of that system.

Table 1. Effective molecular pair correlation energies[a]

k, l[b]	Neutral	Cation	Anion
$1\sigma_g, 1\sigma_g$	−0.614	−0.613	−0.614
$2\sigma_g$	−0.054	−0.058	−0.051
$3\sigma_g$	−0.044	−0.047	−0.042
$1\sigma_u$	−0.614	−0.613	−0.614
$2\sigma_u$	−0.035	−0.039	−0.032
π_u^+	−0.053	−0.054	−0.053
π_u^-	−0.053	−0.054	−0.053
π_g	—	—	−0.053
$2\sigma_g, 2\sigma_g$	−0.326	−0.435	−0.254
$3\sigma_g$	−0.429	−0.469	−0.394
$1\sigma_u$	−0.054	−0.058	−0.051
$2\sigma_u$	−0.361	−0.402	−0.303
π_u^+	−0.380	−0.423	−0.337
π_u^-	−0.380	−0.423	−0.337
π_g	—	—	−0.337
$3\sigma_g, 3\sigma_g$	−0.477	−0.480	−0.476
$1\sigma_u$	−0.044	−0.046	−0.042
$2\sigma_u$	−0.448	−0.460	−0.439
π_u^+	−0.232	−0.249	−0.222
π_u^-	−0.232	−0.249	−0.222
π_g	—	—	−0.222
$1\sigma_u, 1\sigma_u$	−0.614	−0.613	−0.614
$2\sigma_u$	−0.035	−0.039	−0.032
π_u^+	−0.053	−0.054	−0.053
π_u^-	−0.053	−0.054	−0.053
π_g	—	—	−0.053
$2\sigma_u, 2\sigma_u$	−0.400	−0.420	−0.390
π_u^+	−0.222	−0.261	−0.194
π_u^-	−0.222	−0.261	−0.194
π_g	—	—	−0.194
π_u^+, π_u^+	−0.849	−0.849	−0.849
π_u^-	−0.378	−0.378	−0.378
π_g	—	—	−0.849
π_u^-, π_u^-	−0.849	—	−0.849
π_g	—	—	−0.378

[a] All energies are in eV.

[b] Since $\bar{\varepsilon}_{kl} = \bar{\varepsilon}_{lk}$, only those pairs satisfying $k \leqq l$ relation are given.

into account. This has been computed to be 10.01 eV, about 1.4 eV lower than the experimental energy, using the minimal basis set SCF wavefunctions utilized in Table 1. An "exact" Koopmans' Theorem would replace the ground state SCF wavefunction by its Hartree-Fock counterpart. The sum of $\Delta E(K)^{n\to c}$ and $\Delta E(\text{reorg})^{n\to c}$ is defined as $\Delta E(\text{SCF})^{n\to c}$ and includes the reorganization effect.

This quantity is seen from Table 3 to be an additional 0.7 eV lower than the Koopmans' value, and hence 2.0 eV lower than the experimental quantity. Inclusion of the correlation terms should increase the ionization energy because of the decrease in correlation energy in going to the positive ion. In fact, the

Table 2. Correlation terms in acetylene[a]

State	Parts[b]	E^{σ}_{corr}	$E^{\sigma-\pi}_{\text{corr}}$	E^{π}_{corr}	E_{corr}
Positive ion[c]	A	-5.97	-2.39	-1.23	-9.59
	S	-0.43	-0.68	–	-1.11
	I	-0.62	-0.05	–	-0.67
	T	-7.02	-3.12	-1.23	-11.37
Neutral	A	-5.95	-3.02	-2.45	-11.42
	S	-0.34	-0.70	–	-1.04
	I	-0.37	-0.04	–	-0.41
	T	-6.66	-3.76	-2.45	-12.87
Negative ion[c]	A	-5.94	-3.62	-3.68	-13.24
	S	-0.21	-0.65	–	-0.86
	I	-0.20	-0.03	–	-0.23
	T	-6.35	-4.30	-3.68	-14.33

[a] Energies are given in eV.

[b] Here A stands for "all-external", S stands for "semi-internal", I stands for "internal" and T stands for "total".

[c] Calculated using the reorganized wave functions of Ref. [6].

Table 3. Energy terms involved in formation of acetylene ions[a]

Term		Σ	Π	$\Sigma-\Pi$	Total
$\Delta E\,(\text{corr})^{n\to c}$	b	-0.36	1.22	0.64	1.52
$\Delta E\,(\text{reorg})^{n\to c}$	c	-4.01	-11.88	-15.23	-0.66
$\Delta E\,(\text{SCF})^{c}$	f				-4.12
$\Delta^2 E\,(\text{SCF})^{n\to c}$	g				0.67
$\Delta E\,(K)^{n\to c}$	c				-10.01
$\Delta E\,(\text{SCF})^{n\to c}$	c				9.44
$\Delta E\,(\text{SCF}+\text{corr})^{n\to c}$					10.96
$\Delta E\,(\text{EXP})^{n\to c}$	d				11.40
$\Delta E\,(\text{corr})^{n\to a}$	b	0.31	-1.23	-0.54	-1.46
$\Delta E\,(\text{reorg})^{n\to a}$	c	3.56	27.90	-33.50	-2.04
$\Delta E\,(G)^{n\to a}$	c				9.14
$\Delta E\,(\text{SCF})^{n\to a}$	c				7.10
$\Delta E\,(\text{SCF}+\text{corr})^{n\to a}$					5.64
$\Delta E\,(\text{SCF})^{n}$	e				-4.79
$E\,(\text{HF})^{n}$ (*ab initio*)	e				-2091.20
$E\,(\text{HF})^{n}$ (predicted)					-2091.48
$E\,(\text{HF})^{c}$ (predicted)	f				-2081.32

[a] In eV. See Fig. 1 for definition of terms. Also $\Delta E\,(\text{corr})^{n\to c} = E^{c}_{\text{corr}} - E^{n}_{\text{corr}}$, $\Delta^2 E\,(\text{SCF})^{n\to c} = \Delta E\,(\text{SCF})^{c} - \Delta E\,(\text{SCF})^{n}$, etc.

[b] From Tab. 2.

[c] From Ref. [6]. The values differ slightly from those given in Table 6 of Ref. [6] because $\zeta\,\text{H}_{(1s)} = 1.00$ there, and 1.20 here.

[d] Dibeler, V. H., Reese, R. M.: J. Chem. Phys. **40**, 2034 (1964). The zero point energy correction is neglected.

[e] From Ref. [10].

[f] Calculated from Eq. (7).

[g] Calculated from Eq. (8).

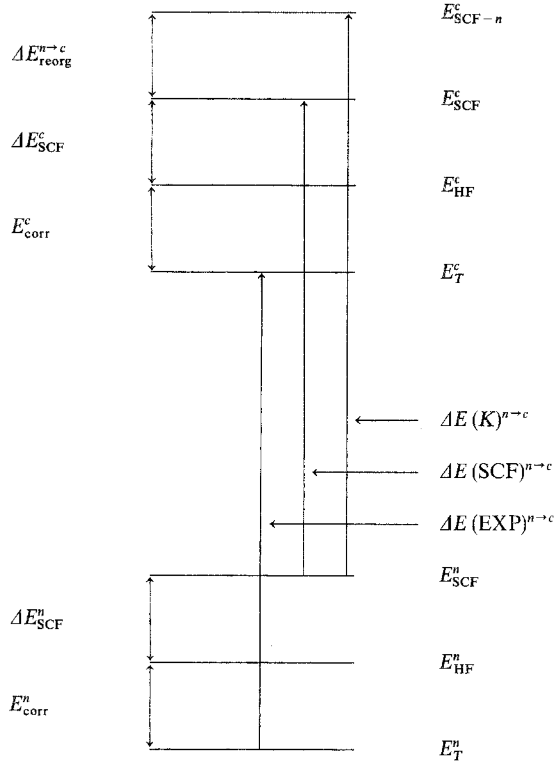

Fig. 1. Energy relationships in ionization. $\Delta E(K)^{n\to c}$ refers to Koopmans' theorem $E^{c}_{\mathrm{SCF}-n}$ the energy of the ionized state calculated from the ground state SCF function. $E(\mathrm{true})^{n}$ and $E(\mathrm{true})^{c}$ are the true energy of the ground and ionized states respectively. A similar diagram holds for electron capture

calculated decrease $\Delta E\,(\mathrm{corr})^{n\to c}$ is greater than the calculated reorganization energy term, ΔE $(\mathrm{reorg})^{n\to c}$. Thus the calculated correlation effects actually do account for most of the discrepancy between $\Delta E(\mathrm{SCF})^{n\to c}$ and $\Delta E(\mathrm{EXP})^{n\to c}$.

Besides correlation and reorganization effects, the degree of goodness of the restricted basis set SCF solutions with respect to exact Hartree-Fock solutions can be considered. This quantity, $\Delta^2 E\,(\mathrm{SCF})^{n\to c}$ in Eq. (4), is

$$\begin{aligned}\Delta^2 E(\mathrm{SCF})^{n\to c} = \Delta E(\mathrm{SCF})^{c} - \Delta E(\mathrm{SCF})^{n} = [E(\mathrm{HF})^{c} - E(\mathrm{SCF})^{c}]\\ - [E(\mathrm{HF})^{n} - E(\mathrm{SCF})^{n}]\,.\end{aligned} \tag{5}$$

We know that

$$E(\mathrm{HF})^{c} = E(\mathrm{true})^{n} + \Delta E(\mathrm{EXP})^{n\to c} - E^{c}_{\mathrm{corr}}\,. \tag{6}$$

Since $E(\mathrm{true})^{n} = E(\mathrm{HF})^{n} + E^{n}_{\mathrm{corr}}$, then

$$E(\mathrm{HF})^{c} = E(\mathrm{HF})^{n} - \Delta E(\mathrm{corr})^{n\to c} + \Delta E(\mathrm{EXP})^{n\to c}\,. \tag{7}$$

Eq. (7) allows “empirical” Hartree-Fock positive ion energies to be obtained analogous to “empirical” Hartree-Fock ground state energies [13].

$E(\mathrm{HF})^c$ is estimated to be -2081.32 eV using McLean and Yoshimine's [11] Hartree-Fock energy for the acetylene neutral ground state. $\Delta^2 E(\mathrm{SCF})^{n\to c}$ can be computed from the observed ionization energy,

$$\Delta^2 E(\mathrm{SCF})^{n\to c} = \Delta E(\mathrm{EXP})^{n\to c} - \Delta E(\mathrm{SCF})^{n\to c} - \Delta E(\mathrm{corr})^{n\to c}. \qquad (8)$$

Utilizing the quantities in Table 3 and the experimental ionization energy, $\Delta^2 E(\mathrm{SCF})^{n\to c}$ is calculated from Eq. (8) to be 0.44 eV, much less than either $\Delta E^c(\mathrm{SCF})$ or $\Delta E^n(\mathrm{SCF})$ using the minimal basis set, optimized atomic exponent SCF functions. This means that for this type of function the ionized state of acetylene is described about as well as the ground state (referring to the Hartree-Fock functions as the standard of comparison), and also that in considering the ionization energy the correlation and reorganization effects are as important as extending the basis set to approach the Hartree-Fock limit.

If the c superscripts in Eq. (4) are replaced by a, then $\Delta E(\mathrm{total})^{n\to a}$ is the electron affinity. There is no analog to Koopmans' Theorem for electron affinities. Since the reorganization, $\Delta E(\mathrm{reorg})^{n\to a}$, and correlation, $\Delta E(\mathrm{corr})^{n\to a}$, are additive, the first term in the negative ion version of Eq. (4) should not give good electron affinities. The calculated sum of the reorganization and correlation energies is -3.50 eV for acetylene, and the magnitude of the terms themselves exceed all measured molecular electron affinities. Although it is clear that neglect of reorganization and correlation effects will lead to much too repulsive electron affinities, the final sum, $\Delta E(\mathrm{SCF})^{n\to a} + \Delta E(\mathrm{corr})^{n\to a}$ is still very large predicting an unstable acetylene negative ion.

The EPCE method can be used to estimate the Hartree-Fock energy of acetylene. The experimental binding energy of acetylene is 17.53 eV [5a]. Adding this quantity to the estimated energy for the separated atoms (found by adding together twice the sum of the Hartree-Fock energy of carbon -1025.51 eV; the estimated correlation energy of carbon -4.30 eV [12] and the energy of hydrogen -13.60 eV) estimates the total energy of acetylene. Subtracting the EPCE value for the correlation energy, -12.87 eV gives the Hartree-Fock energy of acetylene, -2091.48 eV. This is 0.28 eV lower than McLean and Yoshimine's *ab initio* Hartree-Fock energy consistent with the suggestion that given a minimal basis set calculation, an experimentally determined binding energy, and the parameters of the EPCE method, one can predict a good guess for the Hartree-Fock energy [13].

3. Correlation Energies from Minimal Basis Set Configuration

Minimal basis set configuration interaction calculations were performed based on the SCF orbitals [6][2]. In the following discussion, the term "unreorganized" refers to wavefunctions constructed from molecular orbitals determined for the neutral ground state molecule. "Reorganized" wavefunctions have both the linear coefficients which weight the basis functions and the exponents of the basis functions optimized for the ionized states.

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[2] $\zeta = 1.0$ for H 1s AO in these calculations rather than $\zeta = 1.2$ reported for the fully optimized functions in Ref. [6]. Comparison of integrals for the two sets of functions shows that only a slight error is incurred.

The quantities obtained from this calculation are listed in Table 4. The orbital combinations on the left side of the table indicate the particular orbital combinations from which electrons were excited in constructing excited configurations. A total of 108 configurations composed of all possible single and double excitations, were constructed for the neutral ground state and were treated all at once.

For the anion and the cation 300–400 configurations can be constructed because for a particular hole-particle combination there are three or five configurations from the satisfaction of spin statistics in the ions, where one or two configurations in the ground state suffice. Due to the size of the program, it is necessary to calculate the configuration interaction serially for the ions. The criterion by which configurations are selected or rejected is based on energy contributions of each configuration to the eigenvalue calculated. In particular, if ψ is the CI wavefunction and Δ_i the i^{th} SCF configuration in

$$\psi = \sum_{i=i} c_i \Delta_i \tag{9}$$

then,

$$\begin{aligned} E = \langle\psi|H|\psi\rangle &= \sum_i \sum_j c_i c_j \langle\Delta_i|H|\Delta_j\rangle = \sum_i \sum_j c_i c_j H_{ij} \\ &= H_{11} + \sum_{i=2} [c_i^2 (H_{ii} - H_{11}) + 2c_1 c_i H_{1i} + \sum_{j \neq i \neq l} c_i c_j H_{ij}] . \end{aligned} \tag{10}$$

If the magnitude of either $c_i^2 (H_{ii} - H_{11})$ (the diagonal contribution), or $2c_1 c_i H_{1i} + \sum_j c_i c_j H_{ij}$ (the off-diagonal contribution) is greater than 10^{-5} Hartrees, the term is kept to be used in the final calculation for the species. According to this criterion, 100 configurations survived for the positive ion, and 109 configurations for the negative ion. (Four additional configurations are kept for the negative ion since they were the only ones which attempt to describe the $\pi_g^+ \pi_u^-$ correlation). The 100 and 113 configurations were obtained for both the reorganized and unreorganized wavefunctions[3] so that an analysis of the reorganization *vs* the correlation problem could be made.

The correlation energies given in Table 4 are pair-wise correlation energies corresponding to the pair-wise correlation energies in Table 1 so that the entries in both tables can be compared in a direct manner.

Π Correlation. The partitioning technique allows determination of the correlation energy of pairs of electrons and assignment to each configuration a partial energy lowering due to its presence. Each excited configuration, is constructed by replacing one or two of the occupied orbitals in the SCF configuration with one or two virtual orbitals. The correlation between two electrons in the π_u^+ molecular orbital (denoted by π_u^{+2} in Table 4) is described by all configurations in which the π_u^+ orbitals of the SCF determinant are replaced by virtual orbitals and the correlation energy associated with the two

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[3] The SCF energies calculated for the neutral ground state and the unreorganized molecular orbital calculations on the cation and anion are 0.06 eV higher than the values reported in Ref. [6]. The SCF energies reported for the reorganized molecular orbital calculations on the cation and anion are 0.37 eV and 0.12 eV, respectively, more positive than the values in Ref. [6]. We ascribe the discrepancy to accumulated round-off errors in the calculation of the two-electron integrals over molecular orbitals from those over atomic basis functions due to transferring of integrals over the basis set and the coefficients in the molecular orbitals from print-out to cards.

Table 4. Types of correlations and their contributions to the correlation energy

Correlations[g]	Neutral	Cation (reorg)	Cation (unreorg)	Anion (reorg)	Anion (unreorg)
$(\pi_u^+)^2$	– 5.530 E–1	– 6.20 E–1	– 5.88 E–1	– 4.95 E–1	– 5.66 E–1
$\pi_u^+ \pi_u^-$	– 3.54 E–1	– 2.67 E–1	– 2.35 E–1	– 1.98 E–1	– 2.32 E–1
$\pi_g^+ \pi_u^-$	0.0	0.0	0.0	– 9.92 E–6	– 3.16 E–8
Total π	– 1.812E-0	– 1.208E-0	– 1.058E-0	– 8.93 E–1	– 1.029E-0
$\pi_u^3 \sigma_g$	– 8.30 E–2	– 7.48 E–2	– 7.91 E–2	– 6.16 E–2	– 6.06 E–2
$\pi_u^2 \sigma_u$	– 4.25 E–2	– 3.78 E–2	– 3.30 E–2	– 2.73 E–2	– 3.28 E–2
$\pi_u^2 \sigma_g$	– 1.35 E–1	– 1.20 E–1	– 9.86 E–2	– 8.78 E–2	– 1.09 E–1
$\pi_u^1 \sigma_u$	– 1.52 E–4	– 1.37 E–4	– 1.08 E–4	– 7.21 E–5	– 7.36 E–5
$\pi_u 1\sigma_g$	– 1.01 E–3	– 9.94 E–4	– 8.10 E–4	– 5.98 E–4	– 8.15 E–4
Total $\sigma - \pi$	– 1.045E-0	– 9.36 E–1	– 8.46 E–1	– 7.10 E–1	– 8.14 E–1
$(3\sigma_g)^2$	– 1.70 E–1	– 1.62 E–1	– 1.63 E–1	– 1.97 E–1	– 1.51 E–1
$3\sigma_g^2 \sigma_u$	– 1.84 E–1	– 2.08 E–1	– 1.84 E–1	– 1.72 E–1	– 1.48 E–1
$3\sigma_g^2 \sigma_g$	– 1.15 E–1	– 7.95 E–2	– 1.15 E–1	– 1.46 E–1	– 1.19 E–1
$3\sigma_g 1\sigma_u$	– 1.54 E–4	– 1.59 E–4	– 1.15 E–4	– 1.12 E–4	– 9.05 E–5
$3\sigma_g 1\sigma_g$	– 6.05 E–4	– 6.65 E–3	– 6.15 E–4	– 5.00 E–4	– 5.15 E–4
$(2\sigma_u)^2$	– 1.88 E–1	– 1.84 E–1	– 1.75 E–1	– 1.96 E–1	– 1.72 E–1
$2\sigma_u 2\sigma_g$	– 3.86 E–2	– 3.60 E–2	– 4.35 E–2	– 4.15 E–2	– 3.31 E–2
$2\sigma_u 1\sigma_u$	– 3.55 E–4	– 3.69 E–4	– 3.64 E–4	– 3.33 E–4	– 3.27 E–4
$2\sigma_u 1\sigma_g$	– 5.90 E–4	– 5.85 E–4	– 5.60 E–4	– 5.40 E–4	– 5.55 E–4
$(2\sigma_g)^2$	– 3.64 E–1	– 4.14 E–1	– 3.59 E–1	– 3.40 E–1	– 3.70 E–1
$2\sigma_g 1\sigma_u$	– 7.00 E–4	– 5.55 E–4	– 5.75 E–4	– 7.10 E–4	– 7.35 E–4
$2\sigma_g 1\sigma_g$	– 7.20 E–4	– 5.50 E–4	– 5.05 E–3	– 6.35 E–4	– 6.55 E–4
$(1\sigma_u)^2$	– 3.59 E–3	– 3.70 E–3	– 3.46 E–3	– 3.51 E–3	– 3.73 E–3
$1\sigma_u 1\sigma_g$	– 1.05 E–3	– 9.25 E–4	– 9.00 E–4	– 1.12 E–3	– 1.17 E–3
$(1\sigma_g)^2$	– 3.48 E–3	– 3.59 E–3	– 3.34 E–3	– 3.43 E–3	– 3.65 E–3
$3\sigma_g$	– 8.65 E–3	– 1.97 E–2	– 1.29 E–1	– 1.00 E–2	– 3.27 E–1
$2\sigma_u$	– 1.43 E–2	– 3.85 E–2	– 1.50 E–1	– 5.65 E–2	– 2.57 E–1
$2\sigma_g$	– 6.86 E–3	– 1.59 E–2	– 1.15 E–2	– 1.31 E–2	– 2.14 E–2
$1\sigma_u$	– 3.38 E–5	– 1.32 E–4	– 1.01 E–4	– 2.45 E–4	– 7.20 E–4
$1\sigma_g$	– 5.75 E–7	0.0	0.0	– 7.60 E–5	– 2.57 E–4
Total σ	– 1.472E-0	– 1.575E-0	– 1.975E-0	– 1.624E-0	– 2.522E-0
Total E(corr)	– 4.33 E–0	– 3.72 E–0	– 3.88 E–0	– 3.23 E–0	– 4.36 E–0
E (SCF)	–2085.54	–2075.41	–2074.82	–2079.22	–2077.16
E (CI)	–2089.86	–2079.14	–2078.71	–2082.46	–2081.54
ΔE (SCF) [b]	–	10.12	10.72	6.31	8.38
ΔE (CI) [c]	–	10.72	11.16	7.40	8.33
ΔE (reorg) [d]	–	– 6.10 E–1	–	– 2.07 E–0	–
ΔE (corr) adj.[e]	–	–	3.27 E–0	–	– 2.29 E–0
$\%E(\Sigma)$ [f]	22.1	22.4	–	25.6	–
$\%E(\Sigma\pi)$ [f]	73.9	98.1	–	24.3	–
$\%E(\pi)$ [f]	27.8	30.0	–	16.5	–
$\%E$(corr) [f]	33.6	32.7	28.8	22.5	16.0

[a] The contributions are in eV. They are written in E-format, e.g. $1.23\,E-5 = 1.23 \times 10^{-5}$.

[b] The difference $E\,(\mathrm{SCF})^{c,a} - E\,(\mathrm{SCF})^n$.

[c] The difference $E\,(\mathrm{CI})^{c,a} - E\,(\mathrm{SCF})^n$.

[d] The difference $E\,(\mathrm{SCF})^{c,a}$ (reorganized) – $E\,(\mathrm{SCF})^{c,a}$(unreorganized).

[e] The difference $E\,(\mathrm{corr})^{c,a}$(unreorganized) – $E\,(\mathrm{reorg})^{c,a}$.

[f] Calculated with respect to the quantities in Tab. 2.

[g] The notation lists only the holes, e.g. $(\pi_u^+)^2$ represents the sum of the effects of all configurations of the correct symmetry, spin, and angular momentum eigenvalues constructed by the excitation $(\pi_u^+)^2 \rightarrow$.

electrons in the π_u^+ orbital is the sum of the partial energy contributions of all those configurations in which π_u^+ orbitals have been replaced in pairs, since configurations which are formed by replacing, orbitals a and *b* in the SCF determinant describe the correlation between electrons in these orbitals.

In the $\pi_u^+ \pi_u^-$ hole state, the fact that we have fewer electrons correlating helps explain why the contribution is less for the cation than for the neutral molecule. In the case of the anion, configurations constructed to describe correlating electrons in the $\pi_u^+ \pi_u^-$ molecular orbital pair possess two electrons in the π_g^+ orbital. The presence of the two electrons in the π_g^+ orbital destabilizes the configurations. The destabilizing influence of this pair is evidenced by the presence of small coefficients for these configurations as compared to similar coefficients for configurations of the same hole-particle designation in the cation and neutral molecule calculations where the configurations do not have two electrons in the π_g^+ orbital. In this manner, the partitioned energy for this hole pair in the anion will be reduced. The minimal basis set does not allow the construction of additional configurations to alleviate the effects of the pair of electrons in the π_g^+ orbital. In an extended basis set calculation, compensation for this pair of electrons should be possible[4].

$\Sigma - \Pi$ Correlations. The argument used in the case of $\pi_u^+ \pi_u^-$ correlation for the anion is probably also valid in explaining the small $\sigma\pi_u$ correlation energy contributions in that species. Further there is no way to obtain $\sigma\pi_g$ correlation energies in the anion since the minimal basis set does not leave any virtual orbital which can be used and preserve the symmetry[5].

Σ Correlation. Despite having essentially the same sort of hole-particle combinations to describe Σ correlation in the neutral ground state and in the ions, more configurations are available for a particular hole-particle combination in the ions than in the neutral ground state. The increased number of configurations (and, hence, increased flexibility) appear to be the means by which more Σ correlation is obtained for the ions than for the neutral ground state.

4. Reorganized vs. Unreorganized Descriptions

The immediately noticeable difference between the reorganized and unreorganized CI calculations for an ion is in the contributions of the singly excited configurations. In the reorganized calculations, the single excitations should enter in by means of couplings with the doubly excited configurations, since by Brillouin's Theorem, the singly excited configurations, do not interact with the ground configuration. Brillouin's Theorem does not hold however, for the unreorganized wavefunctions; the unreorganized one-electron orbitals are not eigenfunctions of the Fock-operators for the $(n+1)$- and $(n-1)$-electron

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[4] Another quantity which should be improved in an extended basis set calculation is the $\pi_g^+ \pi_u^-$ correlation in the anion. In the minimal basis set, we could only use hole-particle combinations of the form $\pi_g^+ \pi_u^- \rightarrow \sigma_u \sigma_g$, which were inadequate to the task.

[5] Although there are fewer π electrons in the cation than in the neutral molecule, we obtain $\Sigma - \Pi$ correlation energies which are numerically close to the correlation energies for the same hole pairs in the neutral molecule. In the neutral molecule, no matter which $\pi - \sigma$ electron pair is correlated, there is either a π_u^{-2} or π_u^{-2} pair present in the excited configuration. However, two-thirds of the cation configuration lack this correlation which reduces destabilizing effects and encourages better convergence.

Table 5. Singly excited configuration energy contributions[a]

Species	Type of Calc.	E (SCF) "Singles"
Cation	Reorg.	−2075.56
Cation	Unreorg.	−2075.40
Anion	Reorg.	−2079.38
Anion	Unreorg.	−2078.37

[a] Energies in eV.; based on Table 3

ions and direct coupling exists between the single excitations and the ground configuration.

The effect of the single excitations returns some of the electron density to regions close to the molecular framework which are removed from these regions by the dispersive double excitations [14]. The effects of the single excitations using unreorganized wavefunctions show this effect plus the effects of reorganization [15]. Adding together the effects of the single excitations in Table 4 (see Table 5) for both the reorganized and unreorganized wavefunctions, gives a closer correspondence for the cation values than for the anion. Since this value is a guess to the energy of the configuration constructed from the first natural orbitals [16], then it would seem that the first natural orbitals for the Σ system of the cation by either method would be very similar. They would be less similar for the anion. The cation has the advantage of being a relatively well-described bound state and the anion the disadvantage of being a not-too-well-described nonbound state. Concerning the effects of single excitations on the Π system nothing much can be said except that they could be sizable given the significance of reorganization.

In any event, the single excitations are important, even for the reorganized wavefunctions where they contribute 5 to 10% of the Σ correlation energy[6].

5. Comparison of the EPCE and Minimal Basis Set Calculations

Comparison of Tables 1 and 4[7] indicates that the minimal basis set pair correlation energies do not well approximate the EPCE pair correlation energies except for the π_u and $(2\sigma_g)^2$ pairs for which minimal basis set calculations

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[6] The minimal basis set calculation is useful as a guide to what should be done in an extended basis set configuration interaction calculation. Configurations such as single excitations in the π system, and better treatment of the hole combinations in the π system and in the $\Sigma-\Pi$ correlations are desirable.

Secondly, only the valence electrons need be included. As mentioned earlier, $1\sigma_g$ and $1\sigma_u$ orbitals are practically carbon 1s orbitals. It is necessary to include at least 35 configurations for He like ions and 45 configurations for Li like ions if it is desired to obtain over 90% of the total correlation energy [17]. Therefore $1\sigma_g$ and $1\sigma_u$ orbitals may as well be deleted in more extensive calculations.

[7] The details of the atomic contributions in terms of internal, semi-internal, and external correlation are not significant to the total molecular correlation energy. However, incorrect conclusions may be inferred with respect to what one may expect from ab initio calculations by separating Σ, Π, and $\Sigma-\Pi$ correlation energies from the total correlation energy and then further breaking down this partition into contributions due to external, internal, and semi-internal correlation.

are from 50–100% of EPCE values. Why are these particular pairs singled-out for possession of large amounts of the possible pair correlation energies?

In the description of correlation in the π_u pairs, configurations which have the most significant effect are very lowlying ones which contain π_g orbitals substituted for π_u. The effect exercised by these configurations is the introduction of left-right correlation to the π electron system because of the nodal plane perpendicular to the molecular axis in the π_g orbitals, a quite desirable feature. These configurations are probably sufficiently low-lying to account for a very substantial part of the pair correlation energy.

The $(2\sigma_g)^2$ pair is unusual in being the only correlated electron pair among the σ electrons to reproduce the EPCE method result to any large extent. What is unique about this pair as compared to other σ electron pairs?

The $1\sigma_g$ and $1\sigma_u$ orbitals are primarily the inner shell C 1*s* orbitals, hence, the small minimal basis set correlation energies [6] compared to the EPCE results for such pairs.

The $3\sigma_g$ bonding orbital is essentially the bonding orbital between the carbons and the hydrogens. The portion of the $(3\sigma_g)^2$ correlation energy predicted by the minimal basis set is $\sim 1/3$ the ECPE value. This is a significant portion, but it is not as large as one would like for a pair of valence electrons. The correlation which one is trying to describe is between two electrons which can be considered localizable in the C–H σ bonds. In a minimal basis set calculation only the virtual orbitals of σ symmetry can introduce the nodal behavior and localization that is necessary to modify the electron distribution as determined by the $3\sigma_g$ orbital. In an extended basis set calculation in which some π-type basis functions are present on the hydrogens, the density in the C–H bond region should be additionally modifiable. Thus, the poor agreement with the EPCE value is ascribed to the inability of the minimal basis set calculation to modify the C–H bond to any large extent because of lack of π-type functions on the H atoms.

Pairs of σ electrons in which one of the orbitals, or both, is $2\sigma_u$ or $2\sigma_g$ contain at least one orbital in which there is a significant contribution from the valence atomic orbitals on the carbons. These molecular orbitals represent primarily the bonding region between the two carbons, although $2\sigma_u$ contains appreciable H 1*s*. Unlike the $3\sigma_g$ case, the use of configurations in which $2\sigma_g$ and $2\sigma_u$ are replaced by π_g is an effective way of dealing with correlation since these configurations deal effectively with the C–C bonding region.

The $(2\sigma_g)^2$ pair is exceptional; a possible reason may be found in comparison of the $(2\sigma_u)^2$ and the $(2\sigma_g)^2$ pair correlations. For a pair of electrons in the $2\sigma_u$ orbital, some left-right correlation is present by the nodal behavior of the orbital. Excited configurations in which this orbital has been replaced by other functions of *u* symmetry serve merely to modify the details of the $2\sigma_u$ orbital. The effects of such configurations can be reasonably expected to be slowly convergent. The introduction of configurations involving *g* symmetry orbitals can modify the density in the C–C bonding region by the lack of node and by the high density probability of *g* type orbitals in this region. This should significantly modify the left-right correlation. There is however, only one possible configuration involving a *g* symmetry orbital, that with $4\sigma_g$ replacing

$2\sigma_u$ in the $(2\sigma_u)^2$ pair. Compare the $(2\sigma_g)^2$ correlation: there is only one slowly convergent configuration, that constructed by replacing $2\sigma_g$ by $4\sigma_g$. The other configurations formed by the substitution of $3\sigma_u$, and $4\sigma_u$ will introduce left-right correlation into the $(2\sigma_g)^2$ distribution, and thus even at the minimal basis set level the $(2\sigma_g)^2$ pair correlation can be highly effective. The effectiveness of the interaction of configurations in which π_g has replaced $2\sigma_u$ or $2\sigma_g$ is also expected to depend on whether the node in π_g perpendicular to the molecular axis will cause important modification of the probability density or not; according to the foregoing discussion, it should be much more important in the latter case than in the former.

Moskowitz [8a], from an extended Gaussian basis set (EGBS) calculation, calculates as an upper limit for the neutral acetylene correlation energy, -15.02 eV, significantly higher than the EPCE value in Table 2. This correction must contain some portion of the Hartree-Fock energy, since Moskowitz's SCF energy differs from the recently obtained HF energy [11] by 3.05 eV. By utilizing Moskowitz's EGBS estimate for the difference between the SCF and HF limit for C_2 (1.22 eV), a revised EGBS correlation energy is $-15.02+3.05-1.22=-13.19$ eV close to the EPCE value of -12.87 eV.

Compared to CI calculations, the EPCE technique has the merit to reflect intuitions concerning molecular behavior using only atomic quantities as parameters in the molecular problem, a small computation time requirement, and apparent numerical reliability superior to minimal basis set CI.

6. Validity of Π-Electron Approximation in Acetylene

The entries in Table 4 are correlation energies for the hole (occupied MO spin-orbital) pairs given on the left. The particle (virtual, unoccupied MO spin-orbitals) pairs created in order to describe this correlation which conserve the number of σ and π electrons can be considered to be proper configurations within the restrictions of the Π-electron approximation [18]. Those configurations which do not conserve the numbers of σ and π electrons give the error inherent in the wavefunctions constructed in the Π-electron approximation in the same way that excited configurations give the error in the SCF method. These contributions to the hole pair correlation energies are nowhere larger than 10^{-8} eV. Apparently, then, acetylene in the neutral and charged states satisfies the conservation of electron type requirement of the Π-electron approximation.

Acknowledgement. The authors thank the referee for carefully reading and criticizing the manuscript.

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