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CEPA Calculations on Open-Shell Molecules. II. Singlet-Triplet Energy Splitting in π^2 Configurations of Diatomic Molecules

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The CEPA-PNO method is used for calculating the energy difference ΔE_{ST} between the $^3\Sigma^-$ and the $^1\Delta$ states of diatomic molecules in electronic π^2 configurations. An analysis of the contribution of electron correlation to ΔE_{ST} is performed in terms of physically understandable effects such as direct correlation, dynamic spin polarization, semiinternal and internal excitations. It is shown that these effects are of completely different importance for the molecules treated in this study: For C_2 the direct correlation between the two singly occupied π-orbitals is the dominant correlation contribution to ΔE_{ST}; for O_2, S_2, SO the internal excitation $\pi_u^2 \rightarrow \pi_g^2$ is predominant, whereas for NH and PH there is a close competition between the direct correlation and the spin polarization of the underlying σ-orbitals. The basis set dependence of these effects is investigated, in particular for NH. Our final results reproduce experimental values of ΔE_{ST} within 0.05–0.10 eV.

Key words: CEPA – Singlet-triplet splitting – $^3\Sigma^-$ and $^1\Delta$ states of diatomic molecules.

1. Introduction

It is well known that electron correlation can be rather different in ground and excited states of atoms and small molecules. That means, that calculation of electronic excitation energies by the SCF method – to be more specific: by the restricted Hartree–Fock–Roothaan-method – is generally connected with rather large errors. This is particularly so if an electron pair is broken upon excitation;

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since the correlation energy of an isolated electron pair is of the order of 1 eV, one expects the SCF excitation energy to be too small by about this amount. The lowest excited states of He are probably the simplest example for this effect [1].

The situation is different if the two states belong to the same electronic configuration and differ only in the spin coupling of the partly occupied orbitals. Naively, one would expect the correlation energy to be smaller for the state with the higher multiplicity since the Pauli principle keeps the electrons farther apart from each other, thus reducing the correlation of their motion. But the discussion connected with the interpretation of Hund's rule [2] shows that such a picture may be oversimplified. In general, it is quite difficult to get a reliable estimate of how large correlation energy differences can be in these cases. For first and second row atoms and positive ions comparison of the Roothaan–Hartree–Fock results of Clementi and Roetti [3] with experiment [4] shows that the SCF approximation for term splittings in p^2, p^3, p^4 configurations fails by 0.2–1.4 eV. In all cases we find the following inequalities

$$E_{\mathrm{corr}}(^3P) > E_{\mathrm{corr}}(^1D) > E_{\mathrm{corr}}(^1S)$$

$$E_{\mathrm{corr}}(^4S) > E_{\mathrm{corr}}(^2D) > E_{\mathrm{corr}}(^2P).$$

Since – by definition – correlation energies are negative this means that the higher states are more stabilized by correlation than the lower ones, SCF excitation energies are too high. The smallest errors occur for the ^{3}P–^{1}D energy separation in p^2 and p^4 configurations; they are in the order 0.2 to 0.3 eV.

In this paper we present the results of *ab initio* calculations for the triplet-singlet energy separation ΔE_{ST} in π^2 configurations of diatomic molecules. The states studied are

(a) $b\,^3\Sigma_g^-$ and $^1\Delta_g$ (spectroscopically unobserved) excited states of C_2
(b) $X\,^3\Sigma^-$ and $a\,^1\Delta$ states of NH and PH
(c) $X\,^3\Sigma_g^-$ and $a\,^1\Delta_g$ states of O_2, S_2, SO (for SO the subscript g has to be dropped).

For some of these states both theoretical and experimental values of ΔE_{ST} can be found in the literature (see section 3 for references to previous calculations and experiments). They indicate that the SCF results for ΔE_{ST} are too large by about 0.3 eV, very similar to the corresponding ^3P–^1D splitting for p^2 configurations in atoms.

The object of the present paper is a twofold one: First we try to calculate ΔE_{ST} as accurately as possible, aiming at an error not larger than 0.05–0.1 eV, which would be better than almost all previous calculations. Secondly, we try to understand the physical origin of the SCF error and how the correlation contributions to ΔE_{ST} depend on the basis set used. This analysis is the continuation of our previous investigation of dynamic spin polarization effects [5]. Our former analysis, containing NH and O_2 as two examples, was not completely satisfying since not all correlation contributions were included and the treatment was limited to second order perturbation theory.

Singlet-triplet splittings have attracted some recent interest in connection with the question of the electronic structure of organic diradicals [6]. But it has to be stressed that cases like methylene or cyclobutadiene are completely different from the diatomics treated here since they contain the comparison of a closed-shell singlet with an open-shell triplet and since considerable geometry relaxation is involved.

2. Method of Calculation and Basis Sets

We calculate ΔE_{ST} indirectly, i.e. we perform separate calculations for the total electronic energies of the two states and obtain ΔE_{ST} as the difference between them:

$$\Delta E_{\mathrm{ST}} = E(^1\Delta) - E(^3\Sigma).$$

A positive value for ΔE_{ST} indicates that the $^1\Delta$ state lies above the $^3\Sigma$, as it is predicted by Hund's rule.

For the calculation of the total electronic energy the open-shell CEPA method is used which has been described in detail in Part I of this series [7]. Here it is only necessary to emphasize that since we start from separate SCF calculations the orbitals in the two states are slightly different. The RHF calculations for the open-shell singlet states are performed as described in [8].

Our orbital basis sets consist of contracted Gaussian lobe functions. *p*-, *d*-, and *f*-type basis functions are constructed according to the rules given in [9]. We started from Huzinaga basis sets [10, 11] contracted to either double zeta (DZ) or triple zeta (TZ) quality and augmented them step by step by additional functions: *d*- and *f*-type polarization functions on the heavy atoms, *p*-type polarization functions on hydrogen, and diffuse or flat functions (since the letters *d* and *f* are already used, we denote them by r = Rydberg, though they are generally not as diffuse as true Rydberg orbitals). The details of the basis sets used in the subsequent calculations are given in Table 1. Sometimes we also use a shorthand notation ($A, B, \ldots$) in which increasing serial number of the letter in the alphabet indicates increasing basis size. The same letter means the same quality for all molecules (e.g. $B = \mathrm{DZ} + d$).

Only for NH an extended basis, starting from Huzinaga's $11s$, $7p$ set, was used in order to compare our results with those of the best calculations published so far.

3. Overall Results

In this section we present the overall results of our calculations for ΔE_{ST}, an analysis of the correlation effects is given in the following section. In all six molecules considered here the equilibrium distances for the two states differ by

Table 1. Basis sets

Molecule	Name	Type	Contraction of *s*,*p*-part	Exponents of additional functions	Size
C_2	*A*	DZ	$4, 3\times 1; 2, 1$		20
	B	DZ+*d*	(*A*)[a]	*d*: 0.8	30
NH	*D*	TZ	N: $4, 5\times 1; 3, 2\times 1$ H: $3, 2\times 1$		18
	E	TZ+*d*	(*D*)	*d*: 0.9	23
	F	TZ+2*dp*	(*D*)	N: *d*: 1.8, 0.55 H: *p*: 0.9	31
	G	TZ+2*dpr*	(*D*)	N: *s*: 0.06; *p*: 0.05; *d*: 1.8, 0.55 H: *s*: 0.04; *p*: 0.9	36
	H	TZ+ 2*d*1*f*2*p*	(*D*)	N: *d*: 1.8, 0.55; *f*: 1.0 H: *p*: 1.4, 0.35	41
	J	extended +2*d*1*f*2*pr*	N: $5, 6\times 1; 3, 4\times 1$ H: $3, 3\times 1$	N: *s*: 0.045; *p*: 0.038 *d*: 1.8, 0.55; *f*: 1.0 H: *s*: 0.06; *p*: 1.4, 0.35	54
PH	*B*	DZ+*d*	P: $4, 6\times 1; 3, 3\times 1$ H: 3, 1	P: *d*: 0.57	26
	C	DZ+2*dpr*	(*B*)	P: *s*: 0.05; *p*: 0.06; *d*: 0.75, 0.25 H: *p*: 0.55	38
	G	TZ+2*dpr*	P: $6, 7\times 1; 4, 5\times 1$ H: $3, 2\times 1$	P: *s*: 0.045; *p*: 0.028; *d*: 0.75, 0.25 H: *s*: 0.03; *p*: 0.55	47
O_2	*B*	DZ+*d*	$4, 3\times 1; 2, 1$	*d*: 0.8	30
	F	TZ+2*d*	$5, 4\times 1; 3, 2\times 1$	*d*: 2.0, 0.5	48
	G	TZ+2*dr*	(*F*)	*s*: 0.08; *p*: 0.07; *d*: 2.0, 0.5	56
SO	*B*	DZ+2*d*1*d*	S: $5, 6\times 1; 4, 3\times 1$ O: $4, 3\times 1; 2, 1$	S: *d*: 0.95, 0.32 O: *d*: 1.25	44

[a] The symbol (A) means: The same contraction as Basis A of the same molecule.

not more than 0.02 Å. Therefore we did the calculations only for one internuclear separation (which was chosen in most cases close to the equilibrium distance of the triplet ground state). A distinction between vertical and adiabatic excitation energies seemed unnecessary, since for a typical double bond force constant of 10 mdyn/Å we have

$$E(R_e \pm 0.02\ \text{Å}) - E(R_e) \approx 0.012\ \text{eV}$$

which is well below our accuracy for ΔE_{ST}.

3.1. C_2

Both states, $b\ ^3\Sigma_g^-$ and $^1\Delta_g$, belonging to the electronic configuration

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2$$

are excited states of C_2. The $b\ ^3\Sigma_g^-$ state is the second triplet, 0.798 eV (T_e) above the $X\ ^1\Sigma_g^+$ ground state [12, 13], whereas the $^1\Delta_g$ state has not yet been observed since both transitions $X\ ^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ and $a\ ^3\Pi_u \rightarrow {}^1\Delta_g$ are optically forbidden.

Table 2 contains our results together with those of the previous calculations. We have tabulated the total SCF energies and the correlation energies on IEPA, CEPA and PNO-CI levels [7]. In the correlation calculations we started from localized σ-SCF orbitals and included only excitations from the valence shell, i.e. K-shell and K-L-intershell correlations are not taken care of.

The reduction of ΔE_{ST} by electron correlation amounts to about 0.0078 a.u. = 0.21 eV in our best calculation (CEPA, basis B). But a change of the basis set does not alter this result drastically, and the three correlation methods do not differ by more than 0.07 eV. Our final result of 0.803 eV for ΔE_{ST} is in remarkable agreement with the most recent one by Kirby and Liu [17]. It is fair to compare their MCSCF+CI result with our CEPA result (and not with our CI result), since both methods take care of higher order substitutions which are absent in our PNO-CI.

Table 2. $b\ ^3\Sigma_g^- \rightarrow {}^1\Delta_g$ excitation energy of C_2

Reference	Basis	Method	$^3\Sigma_g^-$ (a.u.)	$^1\Delta_g$ (a.u.)	ΔE_{ST} (eV)
14[a]	extended STO	near HF limit	−75.51222	−75.47665	0.968
15[b]	STO, DZ+d	small CI			0.767
16[c]	GL, DZ	small CI	−75.4750	−75.4474	0.75
17[d]	STO, TZ+2d	MC−SCF+CI			0.79
This work[e]	A	E(SCF)	−75.38769	−75.35219	0.966
	(DZ)	E_{corr}(IEPA)	−0.16908	−0.17572	0.786
		E_{corr}(CEPA)	−0.13689	−0.14219	0.822
		E_{corr}(CI)	−0.12742	−0.13163	0.852
This work[e]	B	E(SCF)	−75.43233	−75.39493	1.018
	(DZ+d)	E_{corr}(IEPA)	−0.23397	−0.24234	0.790
		E_{corr}(CEPA)	−0.19975	−0.20760	0.803
		E_{corr}(CI)	−0.18385	−0.18998	0.851

[a] Both states at $R = 1.3693$ Å.

[b] At optimized distances: $R(^3\Sigma_g^-) = 1.4442$ Å, $R(^1\Delta_g) = 1.4661$ Å.

[c] At optimized distances: $R(^3\Sigma_g^-) = 1.402$ Å, $R(^1\Delta_g) = 1.429$ Å.

[d] At optimized distances: $R(^3\Sigma_g^-) = 1.40$ Å, $R(^1\Delta_g) = 1.41$ Å.

[e] Both states at $R = 1.37$ Å; This is close to the experimental equilibrium distance $R = 1.3693$ Å for $b^3\Sigma_g^-$ [18].

Without going too much into details we expect our result to have an accuracy of about 0.05 eV.

3.2. NH *and* PH

The valence electron configuration for the two lowest states of NH and PH can be written as

$$\text{core} \cdot 1\sigma^2 2\sigma^2 1\pi^2$$

where "core" contains the K-shell electrons in the case of NH and the $1s^2 2s^2 2p^6$ electrons of the phosphorus K and L-shell in the case of PH. In our calculations we have correlated only the valence shell electrons and we have used localized σ-orbitals, i.e. 1σ is essentially the lone-pair $2s$ or $3s$ orbital of the heavy atom and 2σ the NH or PH σ-bond, respectively.

For NH, Cade and Huo's early calculations [19, 20] near the HF limit yielded a value of 1.83 eV for ΔE_{ST} which is by 0.26 eV higher than the experimental value of 1.561 eV, observed much later [25]. A number of small and medium-sized CI calculations [21–23] found that correlation seemed to lead to a higher value for ΔE_{ST}, close to 2.0 eV, in sharp contrast to Cade's semiempirical estimate [24] of the correlation contribution.

Our results in Table 3 support these results qualitatively: With a small basis set one does not obtain a reduction of ΔE_{ST} by electron correlation. With increasing basis size the results seem to converge to the experimental value, but one needs rather large basis sets in order to obtain an accuracy of 0.1 eV or better. Note that basis F is already far beyond the standard "DZ + Polarization" quality used in many molecular calculations, but yields a rather poor value for ΔE_{ST}.

Our best result (CEPA, basis J) deviates from the experimental result by still 0.07 eV. It is not obvious what the main source of this error is: According to Cade [24] the relativistic corrections to ΔE_{ST} should be smaller than 0.03 eV. The basis set deficiencies on SCF level may be of the same order of magnitude: Surprisingly, our SCF value for ΔE_{ST} is already 0.07 eV lower than Huo's "near HF value" [20]. This is due to our very low singlet SCF energy, which is 0.0012 a.u. lower than Huo's value. Basis set deficiencies and neglect of higher substituted configurations in our CEPA scheme are probably still the dominating error sources.

The situation is very similar in PH. So far, the most reliable theoretical value for ΔE_{ST} is Cade's semiempirical estimate of 0.95 ± 0.1 eV, starting from an SCF value of 1.25 eV [24]. Exactly the estimated value has been obtained recently by Zittel and Lineberger in laser photoelectron spectrometry experiments [29].

Our results, collected in Table 4, show that it needs again rather large basis sets to reduce the high SCF value for ΔE_{ST} considerably by correlation effects. The error in our best calculation (CEPA, basis G) is still 0.18 eV, this is almost identical to the corresponding result for NH (basis F; the basis sets F and G, differing only in the diffuse basis functions, yield essentially the same results for

Table 3. $X\,^3\Sigma^- \rightarrow a\,^1\Delta$ excitation energy of NH

Reference	Basis	Method[a]	$^3\Sigma^-$ (a.u.)	$^1\Delta$ (a.u.)	ΔE_{ST} (eV)
19, 20[b]	extended STO	near HF limit	−54.97806	−54.91095	1.826
24		semiempirical[c]			1.63 ± 0.1
21[d]	small STO	Valence CI			1.9
22	STO-DZ + *dp*	SD-CI[e]	−55.08397	−55.01029	2.00
22		semiempirical[f]			1.47
23	DZ + *dp*	GVB-CI	−54.99095[g]	−54.91744[g]	2.00[h]
23	DZ + *dp*	POL-CI	−55.04315[g]	−54.97187[g]	1.94[i]
25		exptl.			1.561[j]
This work[k]	*D*	E(SCF)	−54.95286	−54.88508	1.844
	(TZ)	E_{corr}(IEPA)	−0.09242	−0.08912	1.934
		E_{corr}(CEPA)	−0.08138	−0.07891	1.912
		E_{corr}(CI)	−0.07900	−0.07686	1.902
This work	*E*	E(SCF)	−54.96575	−54.89812	1.840
	(TZ + *d*)	E_{corr}(IEPA)	−0.15084	−0.15153	1.821
		E_{corr}(CEPA)	−0.13379	−0.13583	1.784
		E_{corr}(CI)	−0.12864	−0.13079	1.782
This work	*F*	E(SCF)	−54.97018	−54.90308	1.826
	(TZ + 2*d*, 1*p*)	E_{corr}(IEPA)	−0.16872	−0.17072	1.772
		E_{corr}(CEPA)	−0.14984	−0.15338	1.729
		E_{corr}(CI)	−0.14351	−0.14700	1.731
This work	*H*	E(SCF)	−54.97090	−54.90583	1.771
	(TZ + 2*d*1*f*2*p*)	E_{corr}(IEPA)	−0.18149	−0.18460	1.686
		E_{corr}(CEPA)	−0.16333	−0.16803	1.643
		E_{corr}(CI)	−0.15611	−0.16065	1.647
This work	*J*	E(SCF)	−54.97693	−54.91217	1.762
	(extended)	E_{corr}(IEPA)	−0.18504	−0.18850	1.668
		E_{corr}(CEPA)	−0.16601	−0.17078	1.632
		E_{corr}(CI)	−0.15862	−0.16324	1.636

[a] SD-CI: CI with singles and doubles
GVB-CI: Generalized valence bond-CI
POL-CI: Polarization CI.

[b] At experimental distances: $R(^3\Sigma^-) = 1.038$ Å, $R(^1\Delta) = 1.043$ Å.

[c] SCF value of Ref. 20 plus semiempirical estimate of correlation corrections.

[d] Optimized distances: $R(^3\Sigma^-) = 1.12$ Å, $R(^1\Delta) = 1.13$ Å.

[e] Optimized distances: $R(^3\Sigma^-) = 1.041$ Å, $R(^1\Delta) = 1.037$ Å.

[f] CI value of 2.00 eV plus semiempirical estimate of remaining correlation corrections.

[g] At $R = 2.0\ a_0 = 1.0584$ Å.

[h] At optimized distances: $R(^3\Sigma^-) = 1.064$ Å, $R(^1\Delta) = 1.060$ Å.

[i] At optimized distances: $R(^3\Sigma^-) = 1.066$ Å, $R(^1\Delta) = 1.070$ Å.

[j] ν_{00}. Since the values of ω_e and $\omega_e x_e$ are very similar in the two states, T_e is close to ν_{00}.

[k] At $R = 1.037$ Å.

Table 4. $X\,^3\Sigma^- \rightarrow a\,^1\Delta$ excitation energy of PH

Reference	Basis	Method	$^3\Sigma^-$ (a.u.)	$^1\Delta$ (a.u.)	ΔE_{ST} (eV)
26		semiempirical			0.949
24		semiempirical[a]			0.95 ± 0.1
27		semiempirical			0.93
29		experimental			0.950 ± 0.010[c]
This work[b]	*B*	E(SCF)	−341.19299	−341.14467	1.315
	(DZ + *d*)	E_{corr}(IEPA)	−0.09689	−0.09714	1.308
		E_{corr}(CEPA)	−0.09404	−0.09547	1.276
		E_{corr}(CI)	−0.08984	−0.09129	1.275
This work	*C*	E(SCF)	−341.20835	−341.16365	1.216
	(DZ + 2*dpr*)	E_{corr}(IEPA)	−0.13099	−0.13279	1.167
		E_{corr}(CEPA)	−0.12315	−0.12727	1.104
		E_{corr}(CI)	−0.11534	−0.11898	1.117
This work	*G*	E(SCF)	−341.27451	−341.22912	1.235
	(TZ + 2*dpr*)	E_{corr}(IEPA)	−0.13440	−0.13592	1.194
		E_{corr}(CEPA)	−0.12633	−0.13032	1.127
		E_{corr}(CI)	−0.11815	−0.12167	1.140

[a] $\Delta E_{ST} = 1.25$ eV in SCF approximation plus semiempirical estimate of the correlation correction.
[b] At $R = 1.43$ Å.
[c] T_{00}.

ΔE_{ST}). We have also performed a calculation for the *L-M* intershell interaction in PH, but this contributes only 0.003 eV (basis *G*) to ΔE_{ST} and can easily be neglected.

3.3. O_2, S_2 *and* SO

O_2 and SO have the following valence electron configurations

$$\text{core} \cdot 1\sigma^2 2\sigma^2 3\sigma^2 1\pi_u^4 1\pi_g^2$$

where "core" again contains the K-shell electrons of O and the K and L shell electrons of S. In order to save computer time we have further reduced the valence space by including the first two valence orbitals 1σ and 2σ which are the 2*s* electrons of O and the 3*s* electrons of S into the core and correlating only the *p*-type valence electrons. In contrast to the molecules discussed before O_2 and SO have a fully occupied π_u orbital below the half-occupied π_g orbital.

The near Hartree–Fock value for ΔE_{ST} for O_2 is 1.325 eV [14], by about 0.34 eV higher than the experimental value of 0.982 eV [30]. There is a rather large number of CI calculations on ΔE_{ST} in the literature, most of them arrive at values between 1.10 and 1.20 eV. We refer to Ref. 31 containing an up-to-date compilation of these calculations. On the other hand, Lie's MCSCF treatment [32] yields a value of 0.72 eV, i.e. 0.26 eV lower than the experimental value.

Table 5. $X\ {}^3\Sigma_g^- \rightarrow a\ {}^1\Delta_g$ excitation energy of O_2

Reference	Basis	Method	${}^3\Sigma_g^-$ (a.u.)	${}^1\Delta_g$ (a.u.)	ΔE_{ST} (eV)
14[a]	large STO	near HF	−149.6659	−149.6172	1.325
32[b]	STO-4*Z*+2*d*	SCF			1.34
		MC-SCF		−149.69937	0.72
31[c]	STO-TZ+*d*	small CI	−149.9231		1.17
30		exptl.[d]			0.982
This work[e]	*B*	E(SCF)	−149.42892	−149.38141	1.293
	(DZ+*d*)	E_{corr}(IEPA)	−0.30226	−0.32170	0.764
		E_{corr}(CEPA)	−0.22521	−0.23949	0.904
		E_{corr}(CI)	−0.21255	−0.22363	0.991
This work	*G*	E(SCF)	−149.63989	−149.59308	1.273
	(TZ+2*dr*)	E_{corr}(IEPA)	−0.34560	−0.36394	0.774
		E_{corr}(CEPA)	−0.25716	−0.27029	0.916
		E_{corr}(CI)	−0.23973	−0.24965	1.004

[a] At $R({}^3\Sigma_g^-) = 1.208$ Å, $R({}^1\Delta_g) = 1.216$ Å.
[b] At $R = 1.216$ Å.
[c] At $R = 1.217$ Å, 467 configurations for ${}^3\Sigma_g^-$, 463 for ${}^1\Delta_g$.
[d] Adiabatic, T_e.
[e] At $R = 1.21$ Å.

Table 6. $X\ {}^3\Sigma^- \rightarrow a\ {}^1\Delta$ excitation energy of SO

Reference	Basis	Method	${}^3\Sigma^-$ (a.u.)	${}^1\Delta$ (a.u.)	ΔE_{ST} (eV)
34	large STO	SCF[a] near HF limit	−472.40260	−472.36228	1.097
35		Pseudopotential Valence bond[b]			0.64
33	DZ+*d*	SCF[c]	−472.33354		1.029
		CI[d]	−472.51170		0.885
33	[e]	SCF	−472.33550		1.029
		CI	−472.52060		0.847
13,33		exptl.			0.762
This work[f]	*B*	E(SCF)	−472.21631	−472.17856	1.027
	(DZ+*d*)	E_{corr}(IEPA)	−0.25731	−0.27201	0.627
		E_{corr}(CEPA)	−0.19634	−0.20690	0.740
		E_{corr}(CI)	−0.18336	−0.19166	0.801

[a] $R({}^3\Sigma^-) = 1.4811$ Å, $R({}^1\Delta) = 1.4940$ Å.
[b] $R({}^3\Sigma^-) = 1.64$ Å, $R({}^1\Delta) = 1.66$ Å.
[c] T_e value; $R({}^3\Sigma^-) = 1.457$ Å, $R({}^1\Delta) = 1.460$ Å.
[d] T_e value, $R({}^3\Sigma^-) = 1.499$ Å, $R({}^1\Delta) = 1.506$ Å.
[e] DZ+*d* for sulfur, TZ+*d* for oxygen.
[f] At $R = 1.4811$ Å.

Our results with the two basis sets B and G (compare Table 5) agree reasonably well with experiment. They exhibit two characteristic features not observed in the molecules previously discussed: The CEPA results are below the experimental value and the CI values are significantly superior to the CEPA results. Both facts will find a reasonable explanation in the next section.

For SO, there is only one previous CI calculation for ΔE_{ST} [33] with a basis set similar to our basis B, see Table 6. The agreement between our result and experiment is surprisingly good, in particular though basis set B is still very far from the Hartree–Fock limit [34]. As in the case of O_2, the CEPA method seems to overestimate the correlation contribution to ΔE_{ST}.

Our results for S_2 (which are not fully documented here) are again very similar to those for O_2: With the DZ+2d basis we obtain for ΔE_{ST}: 0.829 eV (SCF), 0.625 eV (CEPA), and 0.689 eV (CI) while the experiment yields 0.712 eV [37]. Again the CEPA value is too low, but the CI value nearly perfect. Even the basis set dependence resembles that of O_2: The DZ+d basis yields virtually the same SCF result for ΔE_{ST}, while the CEPA and CI results are lower by 0.02 eV.

4. Analysis of the Correlation Contribution to ΔE_{ST}

In order to understand the origin of the correlation contributions to ΔE_{ST} we have analyzed our CEPA results in some more detail. The following partitioning of the total correlation energy the results of which are collected in Table 7 has proved to give the most lucid interpretation of the correlation effects. (In the classification of the different types of excitation we used the same notation as previously [7]: R, S = doubly occupied; U, V = singly occupied; A, B = virtual orbitals or PNOs.)

(a) External double substitutions: $RR, RS, RU, RV \rightarrow AB$

For these excitations both off-diagonal matrix elements and energy denominators (compare the tables in Part I of this series [7]) are the same for singlet and triplet. Therefore, in second order perturbation theory these contributions to the total correlation energies are the same for the two states, provided that one starts from the same set of orbitals. Since we do separate SCF calculations and go beyond second order perturbation theory we can only expect these contributions to be similar. This is confirmed by the results in Table 7. Though the bulk of the correlation (over 60% in all cases) originates from these contributions they change ΔE_{ST} by much less than 0.1 eV. Unfortunately, the sign of this contribution varies, therefore it is not known in advance whether it will favour the singlet or the triplet.

(b) Direct correlation of the two singly occupied orbitals: $UV \rightarrow AB$

Inspection of the matrixelements [7] shows that these excitations interact with the SCF wavefunctions through the exchange integrals

$$2(A|K_{UV}^{\mp}|B) = (AU|VB) \pm (AV|UB)$$

Table 7. Analysis of correlation contributions to ΔE_{ST} (CEPA-level, all values negative, in 10^{-3} a.u.)

Molecule	C_2	NH	PH	O_2	SO
Basis	*B*[b]	*J*	*G*[c]	*G*	*B*
$^3\Sigma^-$; ext[a]	154.30	120.95	86.24	155.61	127.13
direct	12.48	8.16	6.19	5.04	4.90
s.i.	22.64	11.16	9.17	44.55	29.86
$SP(\sigma)$	11.38	25.75	25.43	1.82	4.06
$SP(\pi)$	—	—	—[d]	28.92	19.79
int.	—	—	—	21.21	10.60
$^1\Delta$; ext	152.80	121.73	86.10	158.53	129.35
direct	22.91	14.92	11.64	9.03	7.96
s.i.	22.76	11.44	9.81	42.18	29.17
$SP(\sigma)$	10.39	22.69	23.44	1.46	3.42
$SP(\pi)$	—	—	—[d]	19.29	14.76
int.	—	—	—	39.80	22.24
Difference[e]					
ext	1.50	−0.79	0.13	−2.92	−2.22
direct	−10.43	−6.76	−5.45	−3.99	−3.06
s.i.	−0.12	−0.29	−0.64	2.37	0.69
$SP(\sigma)$	0.99	3.06	1.99	0.37	0.64
$SP(\pi)$	—	—	—[d]	9.63	5.03
int.	—	—	—	−18.59	−11.64
total diff.	−8.05	−4.77	−3.97	−13.14	−10.56

[a] Abbreviations see text.

[b] Canonical SCF-orbitals, therefore slight differences with respect to Table 2.

[c] With single excitations, therefore slight differences with respect to Table 4.

[d] Since the phosphorus L-shell has not been correlated contributions from $SP(\pi)$ and int. do not exist.

[e] Positive if triplet contribution is larger in absolute value.

with + sign for the singlet and − sign for the triplet, the energy denominators being very similar. The K^- exchange integral is always smaller (in absolute value) than the K^+ integral, since the corresponding density has one additional nodal plane. Thus we expect this contribution to be larger for the singlet which is confirmed by the results in Table 7 and has proved to be valid in most other cases studied so far.

(c) Semiinternal excitations: $RR, RS \rightarrow AU, AV$.

For these excitations more or less the same holds as for the fully external doubles.

(d) Spin polarization terms: $RU, RV \rightarrow AU, AV$.

In a previous publication [5] we have already discussed the "dynamic spin polarization" terms containing true singly substituted determinants originating from excitations of the form

$$RU \rightarrow AU, RV \rightarrow AV$$

But there are also spin polarization excitations of a "screw" form

$$RU \rightarrow AV, RV \rightarrow AU$$

which were believed to give similar contributions to singlet and triplet states. This is not completely correct: In the π^2 molecules the latter excitations always favour the triplets that much that the sum of all spin polarization terms is larger for the triplet states. In C_2, NH, and PH there are only doubly occupied σ-orbitals (SP(σ)); in O_2 and SO the spin polarization of the fully occupied π-orbital, denoted by SP(π), is large, the spin polarization of the much lower σ-orbitals very small.

(e) Internal double substitutions: $RS \rightarrow UV$

For symmetry reasons excitations of this type do exist only for O_2 and SO. Their interaction with the SCF-wavefunction is given by the matrixelement

$$2(R|K^{\pm}_{UV}|S) = (RU|VS) \pm (RV|US)$$

where again the + sign holds for singlet and the − sign for triplet states. Again, the K^+ operator has larger matrixelements, therefore this contribution favours the singlet.

A closer inspection of Table 7 shows that the main correlation contribution to ΔE_{ST} is different for molecules differing in the electronic structure of the underlying doubly occupied orbitals:

(a) For C_2 the dominating contribution to ΔE_{ST} is the direct correlation of the two π-orbitals, lowering the singlet by about 10^{-2} a.u. relative to the triplet. All other contributions are nearly identical. The direct correlation is very large since three valence orbitals are completely unoccupied and available for correlation: $1\pi_g$ and $3\sigma_u$.

(b) For O_2 and SO the internal double substitutions yield the dominating correlation contribution, all other contributions are smaller and cancel to a large extent. Since the matrixelements for the internal double substitutions involve only occupied SCF orbitals this contribution is already obtained with an appropriate SCF basis set. This contribution is so large because of both a large matrixelement and a small energy denominator for the $\pi_u^2 \rightarrow \pi_g^2$ excitation.

It has to be noted that our CEPA scheme seems to become unreliable for exceptionally large semiinternal or internal correlation contributions. The reason is that violations of the Pauli principle become important whenever unlinked clusters of large semiinternal or internal substitutions are treated with the simple CEPA-2 approach. Therefore, the CEPA value for the internal substitution in O_2 is too high, leading to too small a value for ΔE_{ST}. This effect is less pronounced in SO. (A CEPA version correcting for this drawback is in progress.)

For O_2, basis G, the matrixelement coupling the SCF-wavefunction with the internal double substitution and the corresponding CEPA and CI coefficients

Table 8. Basis set dependence of the direct correlation and spin-polarization of NH (CEPA level, all values negative, in 10^{-3} a.u.)

Basis	Contribution	$^3\Sigma^-$	$^1\Delta$	Difference[a]
D	direct	3.75	7.73	−3.98
(TZ)	*SP*(σ)	7.60	0.00	7.60
	total diff.[b]			2.47
E	direct	6.91	12.52	−5.61
(TZ+*d*)	*SP*(σ)	23.49	19.00	4.49
	total diff.			−2.05
F	direct	7.74	14.14	−6.40
(TZ+2*dpr*)	*SP*(σ)	25.37	21.51	3.86
	total diff.			−3.54
H	direct	8.12	14.63	−6.51
(TZ+2*d*1*f*2*p*)	*SP*(σ)	25.91	22.98	2.93
	total diff.			−4.70
J	direct	8.16	14.92	−6.76
(extended)	*SP*(σ)	25.75	22.69	3.06
	total diff.			−4.77

[a] Positive if triplet contribution is larger in absolute value.

[b] Including all other correlation contributions; compare Table 3.

are: 0.1582 a.u., −0.134, −0.107 ($^3\Sigma_g^-$); 0.1942 a.u., −0.205, −0.158 ($^1\Delta_g$). They depend only very slightly on the basis.

(c) Finally, for NH and PH the situation is rather difficult because there is a nearly complete compensation of direct correlation and σ-spin-polarization. This cancellation is extremely basis set dependent as can be seen from Table 8, such that only an extended basis set can yield a reliable value for ΔE_{ST}. In particular, if no δ-orbitals are included in the basis all spin polarization terms are zero, except for the term with the exchange integral

$$(\sigma|K_U+K_V|A)=(\sigma U|VA)+(\sigma V|UA)$$

which is only present in the triplet. Thus, small basis sets overestimate the spin polarization for the triplet and lead to too high values for ΔE_{ST}.

5. Conclusions

The results of our analysis of correlation contributions to ΔE_{ST} in π^2 configurations of diatomic molecules can be summarized as follows:

(a) Though external and semiinternal substitutions cover 70–80% of the total correlation energy in either state their contribution to ΔE_{ST} is rather small, in none of the molecules treated here larger than about 0.05 eV. In most cases the singlet state is stabilized by these substitutions more than the triplet, but it seems impossible to rationalize the sign of this effect.

(b) The direct correlation between the two singly occupied orbitals always favours the singlet; this effect is particularly large if the number of unoccupied valence orbitals is large ("availability of correlating orbitals", see C_2).

(c) Spin polarization of the underlying doubly occupied orbitals always favours the triplet. This is mainly due to the "screw spin polarization terms" while the "dynamic spin polarization" generally leads to a larger stabilization of the singlet as it has been discussed before [5]. The spin polarization contribution to ΔE_{ST} is large only for O_2, S_2 and SO where the fully occupied π_u orbitals can be easily polarized by the π_g electrons (large exchange integral).

(d) For symmetry reasons internal substitutions do exist only for O_2, S_2 and SO among the molecules treated here. In these cases they yield the predominant correlation contribution to ΔE_{ST}, stabilizing the singlets by more than 0.3 eV with respect to the triplets.

The results of our calculation indicate that CEPA results for excitation energies are accurate to about 0.05–0.10 eV provided one can afford a sufficiently large basis set. This seems to be no problem in cases where one type of correlation contribution dominates. In NH and PH, however, there is a nearly complete cancellation of different effects; henceforth a rather large basis is needed for a reliable result. Further, we observe that the CEPA results for excitation energies are superior to CI results, with the exception of O_2 and SO for which the CEPA-2 scheme [7] is inappropriate for the large correlation contribution of the internal substitution.

The molecules C_2, NH and PH, O_2 and SO can be considered as prototypes since we expect similar correlation effects in isoelectronic or isovalence-electronic molecules such as CH^-, OH^+, SiH^-, NF, PF etc. Rydberg states, however, may behave differently as we have shown in a recent analysis of correlation effects in Rydberg states of H_2O [36].

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