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On the accuracy of correlation energy calculated by the correlation factor method: first- and second-row atoms

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Summary. The correlation energy of two- and four-isoelectronic series, a representative example for which the existing spin-density functionals fails, is calculated using the Colle and Salvetti method, considering mono- and multideterminantal wave functions. The results are in agreement with experimental data, and show the potentiality of this method when it is applied to wave functions including the most relevant configurational features. Also, results for the ionization energies and electron affinities of first- and second-row atoms are reported.

Key words: Correlation energy — Functional density — Correlation factor — Ionization energies — Electron affinities

Introduction

Recently several authors have reported very good results for the first ionization energies (IE) and electron affinities (EA) of light atoms, obtained by calculating the correlation energy (CE) within the density functional model [1–5]. Contrarily, other works have shown the inability of such methods to describe correctly the Z-dependence of the correlation energy for the isoelectronic series of two and four electrons [6, 7].

In [7] the results obtained with the Colle and Salvetti method (CS) [8], using a Hartree–Fock wave function, are discussed. This method gives a correct description of the two-electron series, but fails in the four-electron series. Our experience in previous studies [9] points out that the reason for this failure must be in the incorrect selection of the zero-order wave function, since, for the last series, the $2s$ and $2p$ orbitals have a strong interaction, and a small configuration interaction can give a wave function adequate for the estimation of correlation energy using the CS method. However, the results of other methods do not depend on the zero-order wave function used.

The aim of this paper is to show the potentiality of the second-order matrix dependent CS method when it is used in conjunction with a suitable zero-order wave function. For this purpose we have selected the helium and beryllium isoelectronic series, using mono- and multi-determinantal zero-order wave functions. Also we calculate the CE contributions to ionization energies and electron affinities of the first- and second-row atoms.

Wave functions and basis sets

Although a high quality basis set is not required to calculate the CE [7], it becomes essential to estimate the total energy because Hartree–Fock results are very sensitive to basis sets. Two different basis set groups have been used here: Dunning's contracted $(5s, 3p)$ [10] and the 6-311G** by Pople et al. [11]. The former set is a good choice for the present problem and it has been used for species B to Ne; however, as it does not include p-type functions for H to Be, the latter was used for them, and for the second-row. Due to the need of p-type functions in the multi-configurational calculations, we have employed the 6-311G** basis set for the two- and four-electron series.

The mono-determinantal wave function is an unrestricted Hartree–Fock (HF); for the multi-determinantal wave function we have selected a generalized valence bond (with perfect pairing) (GVB-PP) taking as configurations the $1s^2 2s^2$ and the three closed shell biexcitations $2s^2 \rightarrow 2p_q^2$.

Results and discussion

Tables 1 and 2 give the results for the isoelectonic series. In Table 2 the CE(CS) values are the sum of the CE calculated with the CS method and the difference between the GVB-PP and HF energy. Also, results of Perdew's and Becke's functionals [12, 13] (P and B, respectively) are included for comparison. These functionals provide the best results for the present systems between a large set of density functionals [12–22]. Experimental CE values are taken from [23].

The CS results agree qualitatively with experimental data in both series. The CEs obtained have "quasi-constant" values for the two-electron series, but they increase along the four-electron series, leading to a substantial improvement when compared with the results from the other two functionals and those of the literature [7].

We have calculated the CE for each atom of the first and second row and also for the corresponding cation (X^+) and anion (X^-). The results are shown in Tables 3 and 4, respectively, showing, for neutral atoms, the good results of CS method in respect to the other methods. In Tables 5 and 6, the calculated IE and EA values are shown, both including CE and without it. The HF energies

Table 1. SCF energy (E(RHF), in Hartrees) and correlation energy (CE, in mHartrees) for the He-series. The relative error is between parentheses

Sist.	−E(RHF)	−CE(CS)	−CE(P)	−CE(B)	−CE(exp.)
H	0.46667	33.68 (−15.4)	45.26 (13.7)	29.13 (−26.8)	39.8
He	2.85990	41.59 (−1.2)	43.93 (4.3)	41.92 (−0.4)	42.1
Li	7.23584	43.87 (0.9)	45.39 (4.3)	49.84 (14.6)	43.5
Be	13.61037	44.20 (−0.2)	48.62 (9.8)	54.60 (23.3)	44.3
B	21.98489	43.85 (−2.1)	53.18 (18.7)	57.80 (29.0)	44.8
C	32.35939	43.26 (−4.1)	58.53 (29.8)	60.08 (33.2)	45.1
N	44.73373	42.59 (−6.0)	64.41 (42.2)	61.81 (36.4)	45.3
O	59.10791	41.92 (−8.1)	70.59 (54.8)	63.16 (38.5)	45.6
F	75.48190	41.23 (−9.6)	76.93 (68.7)	64.24 (40.9)	45.6
Ne	93.85570	40.56 (−11.2)	83.34 (82.4)	65.14 (42.5)	45.7

Table 2. SCF energy (E(RHF) and E(GVB), in Hartrees) and correlation energy (CE, in mHartrees) for the Be-series. The relative error is between parentheses

Sist.	−E(RHF)	−E(GVB)	−CE(CS)	−CE(P)	−CE(B)	−CE(exp.)
Li	7.42162	7.44981	76.73 (5.8)	83.41 (15.0)	72.80 (0.4)	72.5
Be	14.57187	14.61561	96.52 (2.2)	93.70 (−0.7)	92.48 (−2.0)	94.4
B	24.23517	24.29365	108.76 (−3.2)	101.08 (−10.0)	106.59 (−5.1)	112.3
C	36.40448	36.47640	119.22 (−6.0)	108.35 (−14.6)	116.98 (−7.7)	126.8
N	51.07520	51.15947	127.53 (−9.7)	115.60 (−18.1)	124.82 (−11.6)	141.2
O	68.24250	68.33832	134.30 (−13.4)	123.01 (−20.7)	130.91 (−15.6)	155.1
F	87.90557	88.01271	143.23 (−14.9)	130.41 (−22.6)	135.85 (−19.3)	168.4
Ne	110.06195	110.18041	150.94 (−16.8)	137.92 (−24.0)	139.94 (−22.9)	181.4

Table 3. Correlation energies for neutral atoms, in mHartrees. The relative error is between parentheses

Sist.	−CE(P)	−CE(B)	−CE(CS)	−CE(exp.)
H	2.7 (2.7)	0.0 (0.0)	0.0 (0.0)	0.0
He	43.9 (4.6)	41.9 (−0.2)	41.6 (−1.0)	42.0
Li	52.7 (16.1)	55.2 (21.6)	51.6 (13.7)	45.4
Be	93.7 (−0.3)	92.5 (−1.6)	92.7 (−1.4)	94.0
B	125.7 (1.3)	125.3 (1.0)	125.6 (1.3)	124.0
C	160.3 (3.3)	162.3 (4.7)	160.9 (3.7)	155.1
N	197.0 (5.9)	201.7 (8.4)	197.3 (6.0)	186.1
O	260.6 (2.7)	261.7 (3.1)	258.7 (1.9)	253.9
F	324.8 (2.8)	325.9 (3.1)	318.0 (0.6)	316.0
Ne	389.1 (2.1)	391.1 (2.7)	375.3 (−1.5)	381.0
Na	414.4 (7.4)	419.2 (8.6)	400.8 (3.8)	386.0
Mg	464.8 (8.6)	465.7 (8.8)	450.9 (5.3)	428.0
Al	506.0 (10.2)	504.0 (9.8)	486.1 (5.9)	459.0
Si	550.7 (11.5)	545.6 (10.4)	523.3 (5.9)	494.0
P	596.2 (14.4)	588.9 (13.0)	562.1 (7.9)	521.0
S	663.5 (11.5)	651.4 (9.5)	624.0 (4.9)	595.0
Cl	731.4 (9.6)	717.7 (7.6)	684.2 (2.6)	667.0
Ar	802.2 (9.6)	784.9 (7.2)	742.6 (1.5)	732.0

Table 4. Correlation energies for cations (X^+) and anions (X^-), in mHartrees

	Cations (X^+)			Anions (X^-)		
Sist.	−CE(P)	−CE(B)	−CE(CS)	−CE(P)	−CE(B)	−CE(CS)
H	0.0	0.0	0.0	45.2	29.1	33.7
He	−2.1	0.0	0.0	69.7	69.8	68.1
Li	45.4	49.8	43.9	83.4	72.8	72.5
Be	55.2	63.3	60.9	116.5	105.3	104.0
B	101.4	106.5	106.0	148.7	139.7	137.4
C	133.7	141.0	141.2	186.0	180.0	175.4
N	168.8	178.7	176.8	246.9	238.4	238.0
O	206.2	218.2	213.0	308.7	301.2	297.5
F	273.2	280.2	274.1	371.5	366.2	356.0
Ne	339.5	345.5	333.0	416.5	417.5	403.5
Na	406.3	411.5	389.9	443.7	435.9	420.9
Mg	429.7	439.9	420.8	484.3	474.6	457.3
Al	481.9	489.3	473.0	527.2	515.9	494.3
Si	524.1	527.4	508.3	575.3	560.6	533.9
P	568.3	569.1	546.4	640.2	620.8	595.7
S	615.3	613.4	585.4	706.8	684.8	656.7
Cl	683.6	677.8	646.6	775.6	752.7	716.9
Ar	754.3	744.4	705.7	829.9	812.1	767.7

Table 5. First ionization energies for H to Ar. SCF results (HF), SCF with correlation energy correction of Perdew, Becke and Colle–Salvetti (CE(P), CE(B), CE(CS)) respectively. All values are in eV

Sist.	CE(P)	CE(B)	CE(CS)	HF	Exp.
H	13.68	13.61	13.61	13.61	13.60
He	24.70	24.59	24.58	23.45	24.58
Li	5.54	5.49	5.55	5.34	5.39
Be	9.09	8.84	8.91	8.04	9.32
B	8.59	8.44	8.47	7.93	8.30
C	11.51	11.37	11.32	10.79	11.26
N	14.73	14.58	14.52	13.96	14.54
O	13.37	13.07	13.13	11.89	13.61
F	17.12	16.96	16.91	15.72	17.42
Ne	21.19	21.09	21.00	19.84	21.56
Na	5.17	5.16	5.25	4.95	5.14
Mg	7.57	7.32	7.43	6.62	7.64
Al	6.16	5.91	5.86	5.51	5.98
Si	8.38	8.15	8.06	7.66	8.15
P	10.80	10.58	10.47	10.04	10.55
S	10.35	10.06	10.08	9.03	10.36
Cl	13.09	12.88	12.82	11.80	13.01
Ar	16.08	15.88	15.78	14.78	15.76

Table 6. Electron affinities for H to Ar as Table 5

Sist.	CE(P)	CE(B)	CE(CS)	HF	Exp.
H	0.83	0.46	0.59	−0.33	0.75
He	−21.49	−21.43	−21.47	−22.19	Unstable
Li	0.71	0.36	0.45	−0.12	0.62
Be	−0.58	−0.85	−0.89	−1.20	Unstable
B	0.36	0.12	0.05	−0.27	0.28
C	1.25	1.03	0.94	0.55	1.26
N	−0.79	−1.15	−1.04	−2.15	Unstable
O	0.77	0.53	0.52	−0.54	1.46
F	2.63	2.46	2.40	1.36	3.40
Ne	−20.22	−20.24	−20.19	−20.96	Unstable
Na	0.68	0.34	0.43	−0.12	0.55
Mg	−0.36	−0.65	−0.72	−0.89	Unstable
Al	0.61	0.36	0.25	0.03	0.44
Si	1.63	1.36	1.24	0.96	1.39
P	0.65	0.32	0.37	−0.55	0.75
S	2.08	1.82	1.80	0.91	2.08
Cl	3.78	3.53	3.47	2.58	3.62
Ar	−12.64	−12.66	−12.71	−13.40	Unstable

considered are their limit values; however for He$^-$, Be$^-$, Ne$^-$, Mg$^-$, Ar$^-$ and He$^+$ we have not such data and consequently, the HF energies are those calculated here.

The IE calculated at SCF level are in a reasonable agreement with the experimental data, and the inclusion of CE improves these results.

The EA results are of special interest, showing the importance of including the CE. In fact, the SCF values show a bad behaviour in respect to experiment, with opposite sign for values of H, Li, B, O, Na and P. The calculations with CE agree satisfactorily with experimental trends.

Conclusions

In conclusion, we have showed as the Colle and Salvetti method provides good results when a satisfactory zero-order wave function is used, giving a correct Z-dependence for correlation energies of He and Be series. This method, applied to a HF wave function, provides an improvement in the first ionization energy and electron affinities for the systems studied here as compared with the SCF calculations, being of a quality similar that of other density functional methods, but with a better quantitative results for the correlation energy by hydrogen to argon atoms.

A more extended test on the use of multi-determinantal Colle–Salvetti method for IE and EA calculations is under preparation.

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