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An application of correlation energy density functionals to atoms and molecules

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Four density functionals - including that recently introduced by Perdew ((1986) Phys Rev B33: 8822)—are tested for first-row atoms, hydrides and dimers. Calculated contributions of the correlation energy to the ionization potentials and electron affinities of atoms and to the dissociation energies of molecules are compared with "empirical" values which were reevaluated for this purpose. An improvement over Hartree–Fock is found in all cases if the self-interaction or the gradient correction are included in the density functional, although there is a rather large variation in the accuracy of the predictions.

Key words: Correlation energy — Density functional — First-row atoms — First-row hydrides — First-row dimers

1. Methods

It is well known [1] that the Hartree–Fock (HF) method is quite reliable in predicting some molecular properties such as geometries. There are, however, other properties such as dissociation energies, which need a more refined treatment. This is usually done by using a configuration expansion of the wavefunction. Its slow convergence unfortunately reduces the domain of applicability of such methods.

An alternative has been pointed out by Hohenberg and Kohn [2]. They have shown that the ground state energy of a system can be obtained by minimizing a density functional, $E[n]$:

$$E[n]=F[n]+\int d^3r\, n(r)\cdot v(r) \tag{1a}$$

$$E[n_0]\leq E[n]. \tag{1b}$$

Here n_0 is the exact ground state density of the system, characterized by the external potential v. The functional $F[n]$ does not depend on v and is, in this sense, universal.

One can define a HF energy functional in the same way [3]:

$$E_{\mathrm{HF}}[n]=F_{\mathrm{HF}}[n]+\int d^3r\, n(r)\cdot v(r) \tag{2a}$$

$$E_{\mathrm{HF}}[n_{\mathrm{HF}}]\leq E_{\mathrm{HF}}[n] \tag{2b}$$

(n_{HF} is the HF density). From (1a) and (2a) one can define a universal correlation energy functional:

$$E_c[n]=E[n]-E_{\mathrm{HF}}[n]. \tag{3a}$$

From (1b) and (2b) one obtains that:

$$E_c[n_0]\leq E_c\leq E_c[n_{\mathrm{HF}}] \tag{3b}$$

E_c is the correlation energy in the usual definition [4]

$$E_c=E[n_0]-E_{\mathrm{HF}}[n_{\mathrm{HF}}]. \tag{4}$$

(It can be shown [5] that one also can define a universal density functional yielding Eq. 4).

In most cases one uses spin-density functionals $E_c[n_\uparrow, n_\downarrow]$, where $n_\uparrow$ and $n_\downarrow$ are the spin-up and spin-down densities, instead of the density functionals $E_c[n]$. This generalization was introduced in order to deal with spin-dependent external potentials [3]. For spin-independent external potentials one can argue [6] that a spin direction can be stabilized by an infinitesimal external magnetic field without practically changing the value of the correlation energy.

The use of density functional presents, in spite of its simplicity, a serious drawback: the explicit form of the density functional is not known. In practice, one has to assume a given functional form of $E_c[n_\uparrow, n_\downarrow]$ and then to determine parameters of $E_c[\mathrm{n}_\uparrow, \mathrm{n}_\downarrow]$ from systems were both the density and the correlation energy are known.

The most frequently used choice for $E_c[n_\uparrow, n_\downarrow]$ is the local approximation:

$$E_c[n_\uparrow, n_\downarrow]=\int d^3r\, n(r)\varepsilon(n_\uparrow(r), n_\downarrow(r)) \tag{5}$$

where the function ε depends on the position vector r via $n_\uparrow$ and $n_\downarrow$. It is common to use calculations for the homogeneous electron gas with densities $n_\uparrow$ and $n_\downarrow$ to determine ε. In this case, $n_\uparrow$ and $n_\downarrow$ being spatially constant, ε is the correlation energy per electron. Nowadays good electron gas calculations are available [7] and they were used by Vosko, Wilk and Nusair [8] to fit an analytic expression in $n_\uparrow$ and $n_\downarrow$. The results obtained from Eq. 5 with this parametrization of ε will be denoted by VWN.

Already Hohenberg and Kohn have shown [2] that (5) can be improved by making a gradient expansion. One writes:

$$E_c[n_\uparrow, n_\downarrow] = \int d^3rn \cdot \varepsilon + \int d^3r\, B(n_\uparrow, n_\downarrow)|\nabla n|^2 + \cdots . \tag{6}$$

It is more difficult to determine the function $B(n_\uparrow, n_\downarrow)$ than $\varepsilon(n_\uparrow, n_\downarrow)$. Early attempts [9] were disappointing. Recently Perdew [10] has proposed to use the following form:

$$B(n_\uparrow, n_\downarrow) = B_{\mathrm{RG}}(n) \exp(-b(n)f|\nabla n|n^{-7/6})d^{-1}(m). \tag{7}$$

Here B_{RG} is the electron gas expression for the coefficient of the gradient expansion, which has been determined by Rasolt and Geldart [11] for the paramagnetic case ($n_\uparrow = n_\downarrow = n/2$):

$$\begin{aligned} B_{\mathrm{RG}}(n) &= n^{-4/3}C(n) \\ C(n) &= c_1 + (c_2 + c_3r_s + c_4r_s^2)/(1 + c_5r_s + c_6r_s^2 + c_7r_s^3) \end{aligned} \tag{8}$$

with $r_s = (3/4\pi n)^{1/3}$, $c_1 = 1.667 \cdot 10^{-3}$, $c_2 = 2.568 \cdot 10^{-3}$, $c_3 = 2.3266 \cdot 10^{-2}$, $c_4 = 7.389 \cdot 10^{-6}$, $c_5 = 8.723$, $c_6 = 0.472$, $c_7 = 7.389 \cdot 10^{-2}$ (atomic units).

The exponential factor in (7) is due to the introduction of a cut-off for small k-vectors ($k < f|\nabla n|/n$) in a wave-vector decomposition of $C(n)$, Eq. (8). Such a cut-off procedure was first suggested by Langreth and co-workers [12, 13], in order to approximately account for higher order contributions in the gradient expansion. The function $b(n)$ in the exponent is given by

$$b(n) = (9\pi)^{1/6}C(n \to \infty)/C(n) \tag{9}$$

and the cut-off parameter f has been fitted by Perdew to reproduce the "exact" value of the correlation energy of the Ne atom ($f = 0.11$).

The factor $d^{-1}(m)$ accounts for the spin-dependency of the gradient term:

$$\begin{aligned} d(m) &= 2^{1/3}\{[(1+m)/2]^{5/3} + [(1-m)/2]^{5/3}\}^{1/2} \\ m &= (n_\uparrow - n_\downarrow)/n \end{aligned} \tag{10}$$

This form of $d(m)$ was suggested by Hu and Langreth [13] from considering the scaling properties of the dielectric function of the uniform electron gas in the small k-case.

Improving on this approximation for $d(m)$ seems to be possible, using the results of Rasolt [14] for the gradient expansion of the spin-polarized electron gas in the high density limit. We have tested the effect of such an improvement. It appears to be minor, even smaller than suggested in Ref. [13]. The maximum deviation is 5 per cent for $m = 0.8$. This deviation leads to a change into the right direction for atomic correlation energies, but the change is not large enough (up to 5 mhartrees) to deserve further investigation. In the following, we thus only consider the results using approximation (10). Our notation for the gradient corrected density functional suggested by Perdew (Eqs. 6-10) will be GCP.

Previously to Perdew, Langreth and co-workers [12, 13] have used a simplified form of (7) which corresponds to replacing $C(n)$ by its value in the random-phase approximation (RPA), $C^{\mathrm{RPA}} \approx C(\infty)$ in Eq. (8):

$$B(n_\uparrow, n_\downarrow) = (41472 \cdot \pi^5)^{-1/3} n^{-4/3} \exp(-bf|\nabla n| n^{-7/6}) d^{-1}(m). \tag{11}$$

For the local term (the first one on the right-hand side of (6)) they also suggested a RPA parametrization of ε [15]. Moreover, they introduced a cut-off into the wave-vector decomposition of the local term which is meant to be relevant for finite systems only; this leads to an additional term of the form:

$$(512\pi^5/9)^{-1/3} f^2 \int \mathrm{d}^3 r \, |\nabla n|^2 n^{-4/3} \{[(1+m)/2]^{2/3} + [(1-m)/2]^{2/3}\}. \tag{12}$$

We will denote the results obtained with the method of Langreth et al. (Eqs. 6, 11, 12; $f = 0.17$) by GCL.

Another type of correction to the local approximation (5) which can be applied to atoms and molecules is known as the self-interaction correction. There are different variants. We use here that of Stoll, Pavlidou and Preuss (SPP) [16, 17]:

$$E_c[n_\uparrow, n_\downarrow] = \int \mathrm{d}^3 r \, [n\varepsilon(n_\uparrow, n_\downarrow) - n_\uparrow \varepsilon(n_\uparrow, 0) - n_\downarrow \varepsilon(0, n_\downarrow)]. \tag{13}$$

Within SPP one electron systems have vanishing correlation energy (in contrast to VWN, GCL or GCP).

We now give some details concerning the practical implementation of the methods mentioned above. Our procedure adopted for the calculation of the correlation energy is the following: We first perform a restricted HF calculation, from which we obtain the densities $n_\uparrow(r)$ and $n_\downarrow(r)$. Next we perform the integrations numerically.

The choice of HF densities used for the computation of $E_c[n]$ is not critical. One could obtain a better approximation to n_0 by applying the variational procedure to $E[n] = E_{\mathrm{HF}} + E_c[n]$. This has been previously done for VWN and SPP [18-23] and the result was that the use of this optimized density instead of the HF one practically did not change the results. This can be explained in the following way:

a) the effect of the correlation potential (obtained from the variation of $E_c[n]$) is small compared to that of the Fock potential, so that the density change is relatively small;

b) the conservation of the number of particles implies that $\int \mathrm{d}^3 r \cdot n(r) = N$ for any n. As the integrand in the density functional is not much different from n (between $n \ln(n)$ and $n^{4/3}$) one can expect a cancellation through integration.

For a few systems it is possible to test Eq. (3b), i.e. to compare $E_c[n_0]$ and $E_c[n_{\mathrm{HF}}]$. We have done such a test and found that the two values confining E_c (for the exact density functional) are so close that for practical reasons it is

Table 1. Density dependence of $E_c[n]$. The upper value is obtained with the correlated density of Benesch [24], the lower one within a near-HF density (mhartrees, reversed sign)

System	VWN	SPP	GCP	EXP
H^-	72.0	37.2	38.1	40
	73.6	38.1	39.8	
He	112.8	58.5	44.3	42
	112.9	58.5	44.5	
Li^+	135.2	70.1	46.6	44
	135.3	70.1	46.7	
Ne^{8+}	203.0	104.5	84.7	47
	203.0	104.4	84.5	

sufficient to use $E_c[n_{HF}]$. The values in Table 1 support this statement. There we show the values of $E_c[n_0]$, calculated for VWN, SPP and GCP, with n_0 given by Benesch [24]. The difference between $E_c[n_{HF}]$ and $E_c[n_0]$ is at least one order of magnitude smaller than the errors introduced by the approximate form of the density functional. (As we are not interested in highly ionized systems we do not regard the values for Ne^{8+} as especially critical; there are, however, other errors which will be discussed below.)

For molecules one should use the HF and the exact densities at the respective equilibrium distances, for the determination of E_c. As the HF method is quite successful in generating molecular geometries and the density functionals are quite insensitive to the small changes in the geometry (as for small changes in the densities [21, 22]) we make only a single HF calculation at the experimental geometry [25] for generating the density.

Our previous experience [21, 22] has shown that only moderate basis sets are needed to produce reliable values for $E_c[n_\uparrow, n_\downarrow]$. This can be viewed as an important advantage of the density functional method. However, in order to avoid a supplementary source of uncertainty, we used large contracted Gaussian basis sets [26]: $(8s2p)/[5s2p]$ for H, $(13s4p)/[7s4p]$ for Li and Be and $(13s8p2d)/[7s4p2d]$ for B to F. For negative ions these basis sets were augmented by adding an even-tempered s or p function (for H and Li, viz. B to F). We did not use polarization functions in the ethane calculation.

2. Results

We present the correlation energies obtained with VWN, SPP, GCL [27] and GCP in Table 2. The "empirical" correlation energies have been obtained in the following way:

a) atoms and ions: we subtract the following quantities from the (negative) sum of the experimental ionization energies [28, 29]:
— Dirac-Fock energy

Table 2. Total correlation energies (in mhartrees, with reversed sign)

System	N	VWN	SPP	GCL	GCP	EXP
H	1	22	0	6	2	0
He^+	1	29	0	6	2	0
H^-	2	74	38	50	39	40
He	2	112	59	46	45	42
Li^+	2	135	70	30	47	44
Li	3	151	72	51	54	45
Be^+	3	174	81	34	57	47
Li^-	4	183	95	86	81	73
Be	4	225	116	88	95	94
B^+	4	253	131	78	103	111
B	5	290	147	117	128	125
C^+	5	321	162	105	137	139
B^-	6	315	154	152	149	145
C	6	359	176	150	165	156
N^+	6	391	191	138	175	167
C^-	7	387	184	192	190	183
N	7	430	204	187	206	189
O^+	7	463	219	174	217	195
N^-	8	487	243	248	249	265
O	8	535	267	247	268	258
F^+	8	572	285	236	282	260
O^-	9	591	303	312	310	331
F	9	641	328	311	331	323
Ne^+	9	680	348	300	346	321
F^-	10	696	360	378	373	400
Ne	10	746	386	378	395	387
H_2	2	95	49	55	47	41
LiH	4	219	113	98	93	83
BeH	5	266	130	114	113	93
BH	6	350	181	165	163	153
CH	7	423	215	207	208	199
NH	8	499	249	251	255	243
OH	9	602	309	317	320	316
FH	10	704	364	381	380	387
Li_2	6	330	171	139	134	122
Be_2	8	454	235	196	199	205
B_2	10	592	300	285	285	330
C_2	12	769	398	405	399	514
N_2	14	945	489	511	506	546
O_2	16	1110	570	594	599	657
F_2	18	1302	674	684	697	746
CH_4	10	593	307	372	328	293
NH_3	10	627	325	382	350	338
H_2O	10	664	344	383	365	367
C_2H_2	14	882	457	510	475	476
C_2H_6	18	1088	564	693	613	553

— Breit correction
— vacuum polarization
— self-energy.

These values have been calculated with programs of Grant and co-workers [30, 31] (cf. Table 3).

b) molecules: we add the differences between the HF [32] and experimental [25] dissociation (atomization) energies to the correlation energies of the constituent atoms (cf. Table 4). As we consider only molecules consisting of first-row atoms, we do not expect that the differences considered in b) are altered by relativistic effects by more than $\simeq 10^{-3}$ atomic units.

Of course, there are uncertainties in both the experimental and the HF-limit energy values, used in the calculation of the correlation energy. We believe them to be at most ~0.005 atomic units. The latter value appears as experimental uncertainty for the ionization energy of Ne [28] or in the estimation of the HF-limit of CH_4 and NH_3 [32].

It is worth mentioning that sometimes the correlation energy is defined in a

Table 3. Values used in the calculation of the 'empirical' energies of atoms and ions, in atomic units: Dirac-Fock energy (DF), Breit correction (B), vacuum polarization (VP), self-energy (SE), sum of experimental ionization energies (EXP) [28, 29]

System	DF	B	VP	SE	EXP
He	−2.8618	0.0001	−0.0000	0.0000	−2.9038
Li	−7.4335	0.0003	−0.0000	0.0001	−7.4786
Be	−14.5759	0.0007	−0.0000	0.0003	−14.6693
B	−24.5366	0.0015	−0.0000	0.0007	−24.6593
C	−37.7051	0.0027	−0.0001	0.0015	−37.8574
N	−54.4325	0.0047	−0.0001	0.0026	−54.6140
O	−74.8657	0.0069	−0.0002	0.0044	−75.1126
F	−99.5023	0.0099	−0.0004	0.0068	−99.8092
Ne	−128.6919	0.0154	−0.0006	0.0100	−129.0543
Li^+	−7.2372	0.0003	−0.0000	0.0001	−7.2804
Be^+	−14.2802	0.0007	−0.0000	0.0003	−14.3266
B^+	−24.2452	0.0015	−0.0000	0.0007	−24.3544
C^+	−37.3090	0.0029	−0.0001	0.0015	−37.4436
N^+	−53.9203	0.0044	−0.0001	0.0027	−54.0799
O^+	−74.4287	0.0073	−0.0002	0.0044	−74.6121
F^+	−98.9254	0.0101	−0.0004	0.0068	−99.1689
Ne^+	−127.9647	0.0140	−0.0006	0.0101	−128.2617
Ne^{8+}	−93.9828	0.0121	−0.0006	0.0101	−94.0083
H^-	−0.4879	0.0000	−0.0000	0.0000	−0.5277
Li^-	−7.4290	0.0003	−0.0000	0.0001	−7.5014
B^-	−24.5267	0.0015	−0.0000	0.0007	−24.6696
C^-	−37.7251	0.0027	−0.0001	0.0014	−37.9041
N^-	−54.3538	0.0044	−0.0001	0.0026	−54.6114
O^-	−74.8456	0.0067	−0.0002	0.0041	−75.1663
F^-	−99.5513	0.0107	−0.0004	0.0068	−99.9347

Table 4. Values of Hartree-Fock (HF) [32] and experimental (EXP) dissociation [25, 39] and atomization [32] energies, in atomic units

Molecule	HF	EXP
H_2	0.1336	0.1747
LiH	0.0551	0.0925
BeH	0.0806	0.0795
BH	0.1029	0.1311
CH	0.0915	0.1339
NH	0.0780	0.1325
OH	0.1124	0.1700
FH	0.1617	0.2252
Li_2	0.008	0.039
Be_2	−0.012	0.004
B_2	0.033	0.113
C_2	0.031	0.232
N_2	0.195	0.364
O_2	0.051	0.192
F_2	−0.039	0.061
CH_4	0.531	0.668
NH_3	0.324	0.473
H_2O	0.261	0.370
C_2H_2	0.481	0.644
C_2H_6	0.893	1.133

different way. For example, Pople and Binkley [33] use the spin-unrestricted HF (instead of the restricted HF) value to that scope. With this definition the absolute values may decrease (e.g., by ~0.005 atomic units for C to F). A small difference can also appear when defining the radial part of the np-orbitals. In the numerical Dirac-Fock calculations above there is a difference only between np_+ and np_- orbitals. For the light elements considered this means that all np-orbitals have practically the same radial part. An energy lowering can be produced by relaxing this condition allowing different np-functions for single or double occupation (~0.002 atomic units for O, F and their isoelectronic ions).

Let us now discuss the values presented in Table 2. The most striking feature is the (roughly linear) increase of $-E_c$ with the number of electrons. This trend is common to both the experimental and calculated values.

There are, of course, differences in the correlation energies of isoelectronic systems. Let us first discuss them qualitatively.

a) The separation of the positive charges in the system causes a decrease of density and thus reduces electron correlation (see, e.g. Ne to CH_4). This experimental trend is reproduced by VWN and SPP, not by GCL. This is not a failure of the gradient approximation, as GCP reproduces experimental values even slightly better than SPP.

b) The change of the nuclear charge of the atom, at constant electron number, is related to, but less pronounced than a) Positive ions (Li^+ to F^+) show larger absolute values of the correlation energies than the neutral atoms - a trend which is reproduced by VWN, SPP and GCP. Negative ions are more subtle: experimental values do not show a systematic trend; from He to N the negative ion has a smaller correlation energy than the corresponding isoelectronic neutral atom. For O to Ne the opposite is true. While VWN, SPP and GCP predict a more strongly correlated neutral atom, the contrary is generally observed with GCL.

Even in those cases where the density functional correlation energies exhibit the correct trend with Z, the slope of the curves $E_c(Z)$ is often inaccurate, e.g. for the two-electron systems it is too large, while the opposite is true for four-electron systems [10, 34].

c) The error for the two-electron systems mentioned in b) leads to errors in the core correlation energies for atoms and molecules. Thus molecular correlation energies may be too large compared to isoelectronic atoms within the density functional approximation (see, e.g. Li_2 and C). This error does not appear when considering only valence energies as in pseudopotential calculations.

d) Finally there is a very important effect, namely the structure of the excitation spectrum of the molecule. The role of low-lying states can be easily dealt with in CI-type methods, but is difficult to include in density functionals. We believe that this effect is responsible for the incorrect Z-dependence and the errors in the dissociation energies of C_2, N_2, etc. This effect is of opposite sign to that of c).

Let us now look at differential effects: contributions of the correlation energy to ionization energies (ΔIE), electron affinities (ΔEA) and dissociation energies (ΔD_e). They are shown in Figs. 1-4. A first glance at these figures shows that the

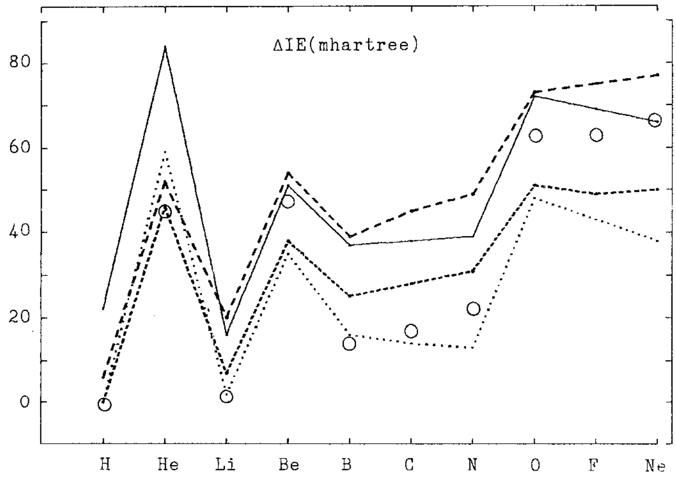

Figure 1. Contribution of the correlation energy to the ionization potential (ΔIE), *full line*: VWN; *dotted line*: SPP; *long-dashed line*: GCL; *short-dashed line*: GCP; *circles*: "empirical"

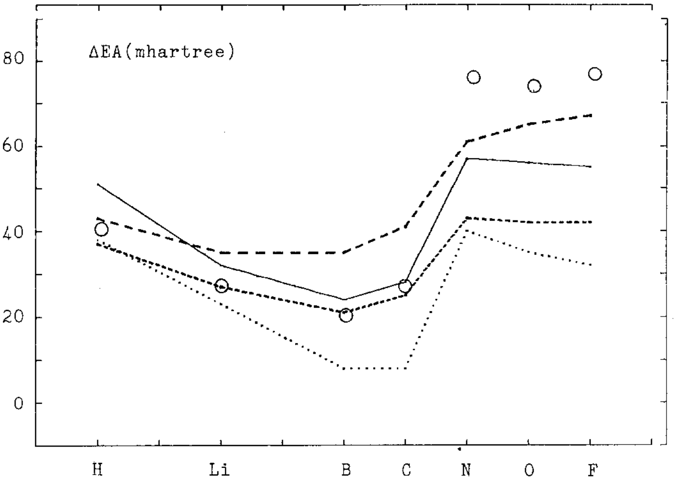

Fig. 2. Contribution of the correlation energy to the electron affinity (ΔEA), *full line*: VWN; *dotted line*: SPP; *long-dashed line*: GCL; *short-dashed line*: GCP; *circles*: "empirical"

contributions to the correlation energies are not overestimated by more than 100% (at least for GCP and SPP, with the exception of ΔD_e of BeH). Thus inclusion of the correlation energy by these density functionals ensures an improvement over HF.

We notice that both experimentally and with density functionals ΔIE and ΔEA show higher values for a change in orbital occupancy from one to two ($Z=2$, 4, 8-10 for ΔIE; $Z=1$, 7-9 for ΔEA; Li has a special behaviour due to the linear Z-dependence) than from zero to one ($Z=1$, 3, 5-7 for ΔIE; $Z=5$, 6 for ΔEA). The magnitude of this effect is underestimated by the density functionals in most

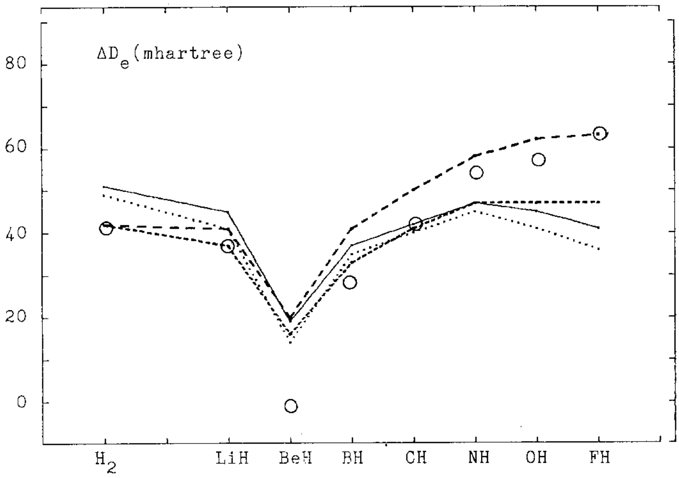

Fig. 3. Contribution of the correlation energy to the dissociation energy of hydrides (ΔD_e), *full line*: VWN; *dotted line*: SPP; *long-dashed line*: GCL; *short-dashed line*: GCP; *circles*: "empirical"

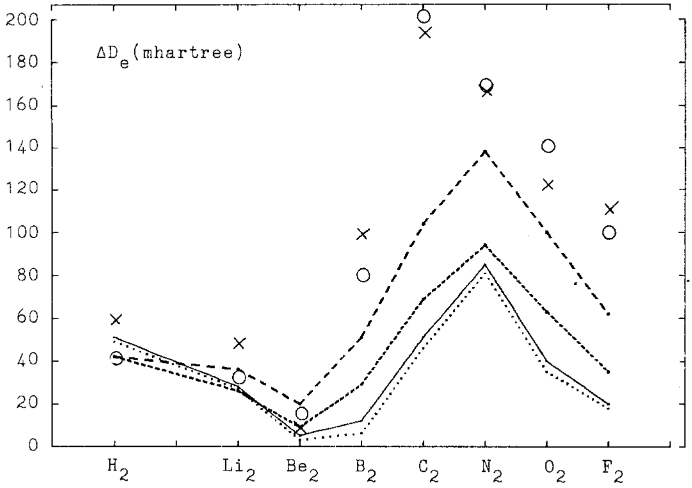

Fig. 4. Contribution of the correlation energy to the dissociation energy of dimers (ΔD_e), *full line*: VWN; *dotted line*: SPP; *long-dashed line*: GCL; *short-dashed line*: GCP; *crosses*: GCP corrected with correlation energies from configurations required for proper dissociation [38]; *circles*: "empirical"

cases. Deviations from experiment of up to 0.03 hartree arise for the changes: $1s \rightarrow 1s^2$, $2s \rightarrow 2s^2$, $2p^3 \rightarrow 2p^4$ (cf., e.g., ΔEA of C and N).

It is difficult to favour one of the methods for computing ΔIE and ΔEA. Some examples: SPP gives the best value for ΔIE (B to N) but decreases with increasing *Z*. GCL is best for ΔEA (N to F) but gives errors of 0.03 hartrees for ΔIE (B to N). GCP is good for ΔEA (H to C) but still produces errors of 40% for ΔEA (N to F). We may recall that it is quite difficult to obtain accurate ΔEA values: a *CI* calculation with a (10*s*9*p*8*d*8*f*6*g*4*h*2*i*) Slater type orbital basis and single and double excitations does not recover more than ~75% of ΔEA for B to F [35].

We now discuss the molecules. For the first row molecules VWN, SPP, and GCP give values which are not far apart. For the hydrides of N to F only the gradient corrected functionals produce ΔD_e which do not decrease from NH to HF. The values obtained are still too low and are comparable in accuracy with CI results with (8s4p1d/4s1p) basis (for N to F/H) [36]. The density functional methods are in error for BeH. Its experimentally negative ΔD_e might be due to an exclusion effect [37].

The most disappointing results seem to be connected with the ΔD_e values for the dimers (Fig. 4). The worst case is C_2, where the density functionals fail by more than 0.1 atomic units. The maximum is experimentally at C_2 and not at N_2, as calculated by the density functional approximations. We believe that this error can be traced back to the one-determinant restriction. In order to support this assertion we look at the values given by Lie and Clementi [26, 38]. They have used a density functional adjusted to reproduce atomic correlation energies (He, Ne). Since there are valence state configurations which contribute to the molecular correlation energy but not to that of the atoms, they proposed to add this supplementary term to the value obtained with their density functional. If we mimic their procedure and correct in the same manner the GCP values, we obtain a significant improvement. The maximum is located at C_2 and not at N_2 any more. The error for C_2 is 0.01 hartrees, for N_2 even less. The values for the cases were a good agreement was found are of course worsened, but the error is still lower than 0.02 hartrees.

3. Conclusions

We have presented correlation energies for first-row atoms and molecules obtained with different density functional approximations, including the recently presented gradient corrected version of Perdew. We cannot give a clear preference to one of the approximations considered. The gradient corrected ones are sometimes superior, but the error can be still too large for chemical applications. It seems that at present density functionals are not able to substitute the role of multideterminantal wave-functions. On the other hand it seems feasible to substantially reduce the error of density functionals by using only a few configurations. The determination of a procedure which avoids double counting of the correlation energy and which is systematically improvable, is still an open question, however.

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