# NON-LOCAL EFFECTS ON ATOMIC AND MOLECULAR CORRELATION ENERGIES STUDIED WITH A GRADIENT-CORRECTED DENSITY FUNCTIONAL

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ABSTRACT. A non-local density functional including gradient corrections has been recently developed by Langreth and Mehl (Phys.Rev. B28, 1809 (1983)), and by Hu and Langreth (preprint RU-85-011). We report on applications of this functional for first-row atoms and molecules (hydrides and dimers). The properties considered are: total correlation energies and correlation contributions to ionization potentials, electron affinities (atoms), and dissociation energies (molecules). The results indicate a significant improvement for total correlation energies and binding energies of diatomic molecules.

## 1. INTRODUCTION

The density-functional method allows, in principle, the calculation of exact ground-state energies, but the universal energy-density functional which would be necessary for this purpose is not explicitly known [1,2]. In the approach, which is most widely used nowadays, a local-density approximation (LDA) is introduced for the exchange-correlation part of the functional [3]. This approach has been remarkably successful for atoms, molecules and solids (cf. e.g. [4]), but a number of systematic errors have been revealed for the exchange as well as the correlation part of the LDA functional (cf. e.g. [5,6]); LDA correlation energies, in particular, are too large in magnitude by about a factor 2. Several corrections to the LDA functional have been suggested in the literature, among them self-interaction (SIC) [7,8] and gradient corrections (GC) [9]. The potential of the latter could not be fully exploited, up to very recently, since the spin dependence of the GC functional was unknown. With the advent of a spin-polarized version [10], this limitation has been removed by now.

In the present paper, we test the performance of the GC functional, in comparison to LDA and SIC, for correlation energies of first-row atoms and molecules. Since differential correlation energies are usually much more important, in applications, than absolute ones, we give not only total correlation energies but also correlation contributions to ionization potentials, electron affinities and dissociation energies.

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## 2.  METHOD

The Hartree-Fock  (HF)  method is used, in our calculations, for generat-
ing (total and partial) electron densities  $n(\vec{r})$, $n_\uparrow(\vec{r})$, $n_\downarrow(\vec{r})$, and den-
sity gradients $\nabla n(\vec{r})$, $\nabla n_\uparrow(\vec{r})$, $\nabla n_\downarrow(\vec{r})$. (Here $\uparrow$ and $\downarrow$ are spin indices,
$n(\vec{r}) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})$). In the HF calculations, finite (contracted)
Gaussian basis sets are employed:  $(8s2p)/[5s2p]$ for the  H atom,
$(13s4p)/[7s4p]$ for Li and Be, and  $(13s8p2d)/[7s4p2d]$ for B to F [11].
For negative ions, a single diffuse basis function is added in each case,
an even-tempered s for H, Li and Be, and a  p function with exponent
taken from [12] for B to F. The calculations are of the restricted
Hartree-Fock  (RHF) type. No spherical restriction is imposed on the Fock
potential of the atoms. The resulting density information is then used as
input for various correlation-energy density functionals.

In the LDA approximation, the functional is

$$E_c^{LDA}[n_\uparrow, n_\downarrow] \;=\; \int \epsilon_c[n_\uparrow(\vec{r}), n_\downarrow(\vec{r})]\, n(\vec{r})\, d^3\vec{r} \tag{1}$$

where $\epsilon_c(n_\uparrow, n_\downarrow)$  is the correlation energy per particle of the homogeneous
electron gas with densities  $n_\uparrow, n_\downarrow$. We took the parametrization of Vosko
et al [13] for  $\epsilon_c(n_\uparrow, n_\downarrow)$,  in our calculations with eq (1).

With the self-interaction correction of [7], the functional reads

$$E_c^{SIC}[n_\uparrow, n_\downarrow] \;=\; E_c^{LDA}[n_\uparrow, n_\downarrow] - E_c^{LDA}[n_\uparrow, 0] - E_c^{LDA}[0, n_\downarrow] \tag{2}$$

Again we employed the Vosko et al parametrization for $\epsilon_c$. The  SIC func-
tional of [8] looks different from that in eq (2), but the results for
the atoms and molecules considered in this work are only marginally dif-
ferent.

The gradient corrected correlation functional [10] reads (in
hartrees)

$$E_c^{GC} \;=\; \int \epsilon_c(n_\uparrow, n_\downarrow) n\, d^3\vec{r} \;+$$
$$+ \; a \int (|\nabla n|^2/n^{4/3}) \; \frac{\exp(-b|\nabla n|/n^{7/6})}{\left[(n_\uparrow/n)^{5/3} + (n_\downarrow/n)^{5/3}\right]^{1/2}} \; d^3\vec{r} \;+$$
$$+ \; 9af^2 \int \left[ (|\nabla n_\uparrow|^2/n_\uparrow^{4/3}) + (|\nabla n_\downarrow|^2/n_\downarrow^{4/3}) \right] d^3\vec{r} \tag{3}$$

with

$$a \;=\; \pi/4(6\pi^2)^{4/3}, \quad b \;=\; (9\pi)^{1/6} f$$

In the LDA part of $E_c^{GC}$, the random-phase approximation (RPA) has to
be used for $\epsilon_c$, since the gradient part has been evaluated in RPA also.
It is argued [14] that the terms beyond RPA in the local and non-local
part of $E_c^{GC}$ would almost cancel. The parametrization of von Barth and
Hedin [15] is employed for $\epsilon_c$ in our present calculations. For the
cut-off parameter f, we take the value of 0.17, which was found to be

Table I

Total correlation energies of atoms (in hartrees),
in the local density approximation (LDA), with a
self-interaction corrected (SIC) and a gradient
corrected (GC) density functional. The 'experimental'
values are taken from a compilation in Ref. [16].

| Atom | LDA | SIC | GC | exp. |
|------|------|------|------|------|
| H | 0.022 | 0. | 0.006 | 0. |
| Li | 0.151 | 0.072 | 0.051 | 0.045 |
| Be | 0.225 | 0.116 | 0.088 | 0.094 |
| B | 0.290 | 0.147 | 0.117 | 0.125 |
| C | 0.359 | 0.176 | 0.150 | 0.158 |
| N | 0.430 | 0.204 | 0.187 | 0.188 |
| O | 0.535 | 0.267 | 0.247 | 0.258 |
| F | 0.641 | 0.328 | 0.311 | 0.324 |
| mean error | 0.183 | 0.015 | 0.007 | - |

Table II

Correlation contributions to atomic ionization
energies (in hartrees), for various density
functional approximations (cf. Table I).
The 'experimental' values are the differences
between the experimental [17] and computed
Hartree-Fock ionization energies.

| Atom | LDA | SIC | GC | exp. |
|------|------|------|------|------|
| H | 0.022 | 0. | 0.006 | 0. |
| Li | 0.016 | 0.002 | 0.020 | 0.002 |
| Be | 0.051 | 0.035 | 0.054 | 0.047 |
| B | 0.037 | 0.016 | 0.039 | 0.013 |
| C | 0.038 | 0.014 | 0.045 | 0.017 |
| N | 0.039 | 0.013 | 0.049 | 0.021 |
| O | 0.072 | 0.048 | 0.073 | 0.062 |
| F | 0.069 | 0.043 | 0.075 | 0.063 |
| mean error | 0.015 | 0.008 | 0.017 | - |

optimum for correlation energies of closed-shell atoms in [9].

The integration in eqs (1) to (3) is done numerically (Gauss-Legendre), with a cut-off for densities $n(\vec{r}) < 10^{-7}$ au .

## 3.   RESULTS

### 3.1.   Atoms

Our results for total correlation energies of the first-row atoms (Li to F) are compiled in Table I.  They are compared to 'experimental' correlation energies, computed from experimental ionization potentials and HF energies, using estimates for relativistic effects and radiation corrections. It is seen that  i) the local density approximation overestimates correlation energies in a conspicuous, but rather well-known way; the overestimation of  LDA  is by a factor  ~3 for  Li ,  and this factor decreases, within the first row, to ~2 for  F ;   ii) the self-interaction correction leads to much better agreement with experiment; the  SIC correlation energies are still too high for the first row, but the mean deviation from experiment is  0.017 hartrees (h) only;   iii) the gradient correction is even slightly better than . SIC ; with the exception of Li , the  GC correlation energies are somewhat too small, with a mean deviation from experiment of  0.008 h .

In Table II, we give results for correlation contributions to ionization energies, $\Delta$IE . They are taken from separate calculations for atoms and corresponding ions. The general trends for $\Delta$IE  are correctly reproduced by all methods. $\Delta$IE is larger for ionization from doubly occupied orbitals than from singly occupied ones and it is larger for ionization from  p  than from  s orbitals. Furthermore it is seen that  i) the  LDA values are too large, by a small amount ($\lesssim$0.01 h) for ionization from a doubly occupied orbital, by significantly larger amounts ($\sim$ 0.02 h) for ionization from singly occupied orbitals; the enhancement of $\Delta$IE from  B  to  N  (by 60 %), and the slight one from  O  to  F , are not well reproduced by  LDA ;   ii) the  SIC values show small errors ($\lesssim$0.01 h) for ionization from singly occupied orbitals, but are significantly too low (by $\lesssim$0.02 h) for doubly occupied ones; the trends within the  p series (B to N , and O to F) are incorrect;   iii) with the  GC functional, the outcome is similar to  LDA : the overestimation of $\Delta$IE is somewhat larger  (with the exception of H); the trends in the p series, however, are remarkably well described by  GC . In contrast to  LDA  and SIC , and in contrast also to experiment, the  GC correlation energies decrease, when going from a neutral atom with atomic number  Z  to the isoelectronic  X$^+$ ion with atomic number  Z+1 (cf. Tables I and II). The influence of the gradient correction is overshooting here.

Correlation contributions to electron affinities, $\Delta$EA , taken again from separate calculations for atoms and ions, are compiled in Table III. The characteristic increase of $\Delta$EA  from  B  and  C  to  N, O  and  F  is well reflected by all methods.  i) the  LDA values are slightly too large (by $\lesssim$0.01 h), if the additional electron in the negative ion occupies an s  or an otherwise unoccupied  p orbital; if, on the other hand, p pairing is achieved in the negative ion, the  LDA estimates are too small

Table III

Correlation contributions to atomic electron
affinities (in hartrees), for various density
functional approximations (cf. Table I).
The 'experimental' values are the differences
between the (recommended) experimental [18]
and computed Hartree-Fock electron affinities.

| Atom | LDA | SIC | GC | exp. |
|------|-----|-----|-----|------|
| H | 0.051 | 0.038 | 0.043 | 0.040 |
| Li | 0.032 | 0.023 | 0.035 | 0.027 |
| B | 0.024 | 0.008 | 0.035 | 0.020 |
| C | 0.028 | 0.008 | 0.041 | 0.027 |
| N | 0.057 | 0.040 | 0.061 | 0.073 |
| O | 0.056 | 0.036 | 0.065 | 0.074 |
| F | 0.055 | 0.032 | 0.067 | 0.076 |
| mean error | 0.011 | 0.023 | 0.010 | - |

Table IV

Correlation contributions to dissociation
energies of first-row hydrides (in hartrees),
for various density functional approximations
(cf. Table I). The 'experimental' values are
the differences between the experimental [19]
and computed Hartree-Fock dissociation en-
ergies [20].

| Molecule | LDA | SIC | GC | exp. |
|----------|-----|-----|-----|------|
| LiH | 0.045 | 0.041 | 0.041 | 0.037 |
| BeH | 0.019 | 0.014 | 0.020 | -0.001 |
| BH | 0.037 | 0.035 | 0.041 | 0.028 |
| CH | 0.042 | 0.040 | 0.050 | 0.042 |
| NH | 0.047 | 0.045 | 0.058 | 0.054 |
| OH | 0.043 | 0.040 | 0.060 | 0.057 |
| FH | 0.041 | 0.036 | 0.063 | 0.063 |
| mean error | 0.011 | 0.012 | 0.007 | - |

(by $\lesssim 0.02$ h);   ii) the  SIC results are acceptable for  s electron affin-
ities, but are too small by up to ~0.04 h  for  p affinities;   iii) the
GC functional yields larger $\Delta$EA than the  LDA functional (with the excep-
tion of the  H atom affinity); the overestimation of $\Delta$EA  for  s  and
singly occupied  p orbitals is now comparable in magnitude to the under-
estimation for the doubly occupied  p case; note, however, that the trend
within the  p series (an increase of $\Delta$EA  from  B  to  C , and from  N
to  F), which is not well described by  LDA  and  SIC , is much better
reproduced with  GC .

## 3.2.  Molecules

We first consider diatomic molecules, and we take the first-row mono-
hydrides and homonuclear dimers as examples, i.e. molecules containing
one or two first-row atoms, respectively. We give results for correlation
contributions to dissociation energies, $\Delta D_e$ , calculated at the experi-
mental bond-lengths $R_e$ [20]. (In the case of  $Be_2$ , we chose the best
available theoretical estimate of  $R_e$ [21] .) Our results for  $\Delta D_e$  are
summarized in Tables IV and V.
     For the hydrides (Table IV), it is seen that  i) the  LDA values
are too large at the beginning of the row and become too small at the
end of the row; the exceptionally large error for  BeH (0.02 h)  has to
do with the exclusion effect; this effect, which cannot be simulated by
an  LDA-type scheme, leads to a nearly vanishing experimental  $\Delta D_e$ for
BeH (cf. e.g. [6] ); the large errors for  OH  and  FH  (again  0.02 h)
may be connected to the difficulties of  LDA  with the description of
the  $O^-$  and  $F^-$ ions (cf. Table III);   ii) the  SIC values are only mar-
ginally different from the  LDA ones; in particular, the experimental
trend of increasing $\Delta D_e$ from  BeH  to  FH  is not correctly reproduced:
a fictitious maximum for  NH  appears both in  LDA and  SIC;  iii) the GC
functional yields consistently higher $\Delta D_e$ values than  LDA  (with the
single exception of  LiH); an important outcome is that the increase of
$\Delta D_e$ is largest at the end of the row, so that the maximum of $\Delta D_e$ for NH
disappears, and the  GC results are in accordance with the experimental
trend.
     For the dimers (Table V), it is seen that  i) the  LDA values have
small errors ($\lesssim 0.01$ h) for  s bonding, but much larger ones for p bond-
ing (up to 0.15 h); the $\Delta D_e$ results are consistently too small in the
latter case; the maximum deviation appears for  $C_2$ , where the experi-
mental $\Delta D_e$ has its maximum (the  LDA maximum is for  $N_2$);   ii) the  SIC
values show no improvement over  LDA ; on the contrary, the $\Delta D_e$ values
are even slightly smaller than  LDA ; the maximum of $\Delta D_e$ is for  $N_2$
(instead of  $C_2$) again, and, as in  LDA , $Be_2$ is not bound at  $R_e$ ;
iii) the  GC functional yields $\Delta D_e$ values which are consistently larger
(except for  $H_2$) than the  LDA ones. For  $H_2$ to  $Be_2$ , $\Delta D_e$ is now only
slightly too high (by $\lesssim 0.005$ h), and the sign of the dissociation energy
is correct now for  $Be_2$ ; for  $B_2$ to  $F_2$ , $\Delta D_e$ is still too small, but
the deviations from experiment are reduced by a factor ~2 compared to
LDA  and  SIC . Our dissociation energies are too low for the dimers  $B_2$
to  $F_2$ . Note that in  LDA calculations with local exchange (instead of
HF exchange) dissociation energies are usually too high [22].

Table V

Correlation contributions to dissociation energies
of homonuclear dimers (in hartrees), for various
density functional approximations (cf. Table I).
The 'experimental' values are the differences be-
tween the experimental [19] and computed Hartree-
Fock dissociation energies, with the exception of
$Be_2$ , where the  CI contribution to the dissociation
energy [21] has been taken.

| Molecule | LDA | SIC | GC | exp. |
|----------|-----|-----|-----|------|
| $H_2$ | 0.051 | 0.049 | 0.042 | 0.041 |
| $Li_2$ | 0.028 | 0.028 | 0.036 | 0.032 |
| $Be_2$ | 0.005 | 0.003 | 0.020 | 0.015 |
| $B_2$ | 0.012 | 0.006 | 0.051 | 0.081 |
| $C_2$ | 0.051 | 0.046 | 0.104 | 0.203 |
| $N_2$ | 0.085 | 0.081 | 0.138 | 0.174 |
| $O_2$ | 0.040 | 0.035 | 0.100 | 0.145 |
| $F_2$ | 0.021 | 0.018 | 0.061 | 0.111 |
| mean error | 0.066 | 0.069 | 0.034 | - |

Table VI

Correlation contributions to atomization
energies (in hartrees) for various density
functional approximations (cf. Table I).
The 'experimental' values are from Ref. [20].

| Molecule | LDA | SIC | GC | exp. |
|----------|-----|-----|-----|------|
| $CH_4$ | 0.15 | 0.13 | 0.20 | 0.14 |
| $NH_3$ | 0.13 | 0.12 | 0.18 | 0.15 |
| $OH_2$ | 0.09 | 0.08 | 0.13 | 0.11 |
| FH | 0.04 | 0.04 | 0.06 | 0.06 |
| mean error | 0.02 | 0.02 | 0.03 | - |

We now turn to polyatomic molecules. Total correlation energies for a number of closed-shell polyatomic molecules have been given in [23] ; by combining these energies with the atomic correlation energies of Table I, the discussion of correlation contributions to atomization energies, $\Delta E_a$ , becomes possible. Results for the isoelectronic series $CH_4$ , $NH_3$ , $H_2O$ , HF are given in Table VI. It is seen that i) LDA and SIC yield similar values; the trend of $\Delta E_a$ is in rough agreement with experiment: the steep increase from FH to $NH_3$ is correctly reproduced, but the slight decrease from $NH_3$ to $CH_4$ is not caught; ii) GC is not superior here to LDA and SIC ; on the contrary, GC seems to unduly favour molecules with a large number of bonds: for $CH_4$ , the overestimation of $\Delta E_a$ is 0.06 h with GC , while it is only 0.01 h with LDA. A similar situation arises for the isoelectronic molecules $C_2H_2$ and $N_2$ . The correlation contributions to the atomization energy should decrease by 0.01 h when going from $N_2$ to $C_2H_2$, but it increases instead by 0.03, 0.02 and 0.06 h , when the LDA , SIC , and GC functionals are used, respectively. The strong overestimation of correlation-energy changes for increasing number of bonds within an isoelectronic series, with the GC functional, could indicate a too small gradient correction in the internuclear region (where the gradient is small).

4.  CONCLUSIONS

The gradient-corrected density functional (GC) of Langreth and coworkers has been tested for the correlation energies of first-row atoms and molecules. It has a distinct advantage over the local-density method (LDA), as far as total correlation energies are concerned: it is comparable in performance here with self-interaction corrected local density functionals (SIC). With respect to correlation contributions to atomic and molecular properties, the GC functional seems to be superior to both LDA and SIC , in general. Some weaknesses of GC are apparent, however, from a consideration of isoelectronic series of atoms and molecules: the gradient correction seems to overshoot for correlation energies of positive ions (high gradient), while it seemingly has too small an effect for internuclear regions (low gradient).

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