

Molecular Correlation Energies Obtained with a Nonlocal Density Functional

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The nonlocal approximation to the correlation energy density functional proposed by Langreth and Mehl [Phys. Rev. B **28**, 1809 (1983)] is applied to molecules. A substantial improvement over the local approximation is observed. However, the errors are larger than in the atomic case.

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Electron correlation effects are known to be important in molecular calculations. There have been, however, only a few attempts to take them into account without doing expensive configuration-interaction calculations. Among them, a very promising method has been the use of density functionals (see, e.g., Ref. 1). Until now, mostly local spin-density calculations were used.

Recently, Langreth and Mehl (LM) have published a nonlocal approximation for the correlation energy functional to be used in non-spin-polarized systems.² Their correction to the local density functional (of von Barth and Hedin³) is given (in hartrees) by

$$a \int d^3r [\nabla n(\vec{r})]^2 [n(\vec{r})]^{-4/3} \\ \times [\exp(-F) + 9f^2],$$

where n is the density, $F = b |\nabla n(\vec{r})| [n(\vec{r})]^{-7/6}$, $a = \pi/8(3\pi^2)^{4/3}$, $b = (9\pi)^{1/6}f$, and f is an adjustable parameter [cf. Eq. (5.1) of Ref. 2]. Langreth and Mehl suggest a value $f \sim 0.15$. Slightly smaller values (0.13) gave better results for surfaces, while larger ones (0.17) were better for atoms. With the latter value for f , atomic correlation energies are reproduced to about 0.005 hartree. The purpose of this Letter is to present LM results for closed-shell molecules.

A comparison is made with the following: (a) "experimental" values; (b) values obtained in the local density approximation, with the parametrization of Vosko, Wilk, and Nusair³ for the correlation energy of the homogeneous electron liquid⁵ (VWN); (c) values obtained in the self-interaction-corrected variant of VWN, with the method of Stoll, Pavlidou, and Preuss⁶ (SPP).

The results are shown in Table I. Some details follow.

(1) All values are for experimental geometries (slight geometry changes do not significantly alter the results).

(2) The integration of the density functional was done numerically (Gauss-Legendre).

(3) The definition used for the correlation energy, E_c , is slightly different from the standard one.⁹ E_c for a given energy density functional is obtained by subtraction of the Hartree-Fock from the given energy density functional both evaluated with the Hartree-Fock density: $E_c = E[n_{\text{HF}}] - E_{\text{HF}}[n_{\text{HF}}]$. In our calculations near Hartree-Fock¹⁰ densities are used (basis sets from Lie and Clementi¹¹; without polarization functions in the case of the C_2H_4 and C_2H_6 molecules). The effect of this definition which omits the self-consistency effect of the correlation potential is negligible when compared to the error of the density functional and small even when compared to the effects due to basis-set limitation and numerical accuracy.¹²

(4) For small, exponentially decaying densities the LM approximation gives positive correlation energies. The Gaussian basis sets used in the calculations and the omission of the correlation potential might also have some influence in the region of small densities. The results presented in Table I were obtained by cutting off the density [for $n(\vec{r}) < 10^{-3}$ a.u.]. Without the cutoff the LM correlation energies increase by typically 0.01 hartree.

(5) We have calculated correlation energies within the LM approximation for both $f = 0.15$ and $f = 0.17$. In the discussion we refer only to the $f = 0.17$ values, since (1) there is no qualitative difference between them, and (2) as for atoms, the $f = 0.17$ results are slightly better quantitatively.

We now proceed to the discussion of the results given in Table I. Let us begin with total correlation energies. Both the nonlocal density functional (LM) and the self-interaction-corrected one (SPP) are much better than that of VWN in all cases. The quality of the LM approximation is comparable to the SPP one: The LM values are generally better for diatomic molecules, while they are definitely worse for the polyatomic ones. Both methods seem to be unable to reproduce the near-degeneracy effects, in the case of the C_2 molecule (cf. also Ref. 1). These effects are also present to a lesser extent

TABLE I. Correlation energies (in 10^{-2} hartree, with reversed sign).

Molecule ^a	Expt. ^b	VWN	SPP	LM ^c	LM ^d
H ₂	4	9	5	6	6
LiH	8	22	11	12	11
Li ₂	12	33	17	17	15
BeH ₂	13 ± 1	33	17	19	18
Be ₂	20	45	23	23	21
BH	15	35	18	19	18
BH ₃	20	46	24	29	27
B ₂ H ₆	43	93	48	62	59
CH ₂	21	48	25	29	28
CH ₄	29	59	31	40	38
C ₂	51	77	40	45	42
C ₂ H ₂	47-48	88	46	56	53
C ₂ H ₄	50-51	98	51	65	62
C ₂ H ₆	55	109	56	75	71
NH ₃	33-34	63	33	42	39
N ₂	54-55	94	49	56	52
H ₂ O	36-37	67	35	42	39
HF	37-39	70	36	42	39
F ₂	73-74	130	67	75	70

^aLowest closed-shell state.^b"Experimental" correlation energies compiled from Refs. 7 and 8.^c $f = 0.15$.^d $f = 0.17$.

in the N₂ and F₂ molecules: The error is, however, nearly compensated within the LM approximation, as the correlation energy values in this approximation are generally too low.

Differences of correlation energies are more important than the absolute values. Here the situation is more more critical and LM and SPP approximations do not always give an improvement over the VWN. We discuss (a) trends in isoelectronic series, and (b) correlation contributions to dissociation energies.

The change in the correlation energies within isoelectronic series is not correctly reproduced: e.g., the changes from CH₄ to NH₃, from NH₃ to OH₂, from OH₂ to FH, and from FH to Ne are experimentally 0.04, 0.03, 0.02, and 0.01 hartree; with density functionals all three changes are nearly equal (~ 0.04 for the local approximations VWN and that of Ref. 3; ~ 0.02 with SPP; and negligible changes for LM).

For dimerizations the LM approximation seems to be superior to the VWN and SPP. A typical case is the Be₂ molecule. While the VWN and SPP approximations predict a small minimum at large interatomic distances, the LM yields an equilibrium distance of about 5 a.u., close to the most recent

configuration-interaction calculations⁸ (also in accordance with exchange-correlation local density functional calculations¹³). The contribution of the correlation energy to the binding energy is in agreement with the best available configuration-interaction estimates.⁸ It is interesting to compare the correlation contributions for the dimerizations of Be, BH₃, and CH₂: The "experimental" values are 0.01, 0.04, and 0.08 hartree, respectively. The LM results (0.01, 0.05, and 0.07) are in quite good agreement, while the SPP values are too small (0.00, 0.01, and 0.01 hartree). Note that in these examples the bonding produced by dimerization is quite different.

The quality of the LM contribution of the correlation energy to chemical reactions of closed-shell molecules is not always as good as in the case of dimerizations. Even if the contribution of the correlation energy to the hydrogenation of the CH₂ molecule to CH₄ is well reproduced (the LM approximation is in error by less than 0.01 hartree) other values for hydrogen-addition reactions are largely overestimated (by up to 0.04 hartree for the hydrogenation of C₂H₂, while the SPP is in error by only 0.01).

Of course, a more significant test would be that

of reactions where the change in correlation energy is more important than in most reactions between closed-shell molecules. Unfortunately, the spin-polarized version of the LM nonlocal density functional is not yet known. The question remains, however, whether near-degeneracy effects could be properly accounted for with such a functional.

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