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A test for the Wilson–Levy correlation energy functional

P. Fuentealba
Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago de Chile, Chile and Centro de Mecánica Cuántica Aplicada (CMCA) [1]*, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago de Chile, Chile*

and

Andreas Savin
Institut für Theoretische Chemie der Universitat Stuttgart, Pfaffenwaldring 55, W-7000 Stuttgart 80, Germany

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The accuracy of the recently developed correlation energy functional of Wilson and Levy is investigated. The correlation contributions to first ionization potentials of first-row atoms, hydrides and dimers, as well as the contributions to the dissociation energies of neutral and ionic hydrides and dimers are calculated and compared with experimental values. It is found that the functional developed by Wilson and Levy represents a positive step in the way to improve the accuracy of density functional models.

1. Introduction

In the few last years, the success of density functional models as a good way to improve Hartree–Fock results has been widely recognized, and they have received considerably more attention. This is a result of the systematic work done by many groups in the study of exchange and/or correlation energy density functionals. They have shown that the calculation of the correlation energy by means of density functional models is much simpler to implement than the traditionally used configuration interaction or perturbation theory techniques while the results are of comparable quality. The whole subject is well reviewed in refs. [1–4]. However, in order to describe the correlation energy effect presented in atoms and molecules more studies are necessary to test the accuracy of the various functionals proposed in the literature.

Of physical and chemical significance are the correlation energy differences, i.e. their contribution to measurable properties. Thus, dissociation energies and ionization potentials are good quantities for testing the accuracy of a model calculation. However, it is well known that in performing energy differences a compensation of errors can occur which could give the impression of a high accuracy. When using correlation energy density functionals, at least for atoms and some molecules, this is not the case. Some of the known correlation energy density functionals give good values for the total correlation energy of neutral atoms but show significant deviations in calculating the ionization potentials. This is often related to near-degeneracy effects which are strongly dependent on the electronic configuration.

This work follows the series of papers by Savin et al. [5–9] in testing correlation energy density functionals, in particular the work by Merkle et al. [9], where the gradient corrected GGA91 density functional developed by Perdew and co-workers [10,11] was investigated. The correlation energy contributions to first ionization potentials of first-row atoms, hydrides and dimers, as well as the contributions to the dissociation energies of neutral and ionic hy-

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drides and dimers were calculated and compared with experimental values. In this Letter, the same sample of atoms and molecules is used in order to test the newly developed correlation energy density functional of Wilson and Levy [12].

2. Methods

Wilson and Levy [12] developed a nonlocal Wigner-like correlation energy functional for electronic systems which was constructed to satisfy certain uniform and nonuniform coordinate-scaling requirements. They proposed the following functional:

$$E_c[n_\alpha, n_\beta] = \int \left(an + \frac{b|\nabla n|}{n^{1/3}}\right) (1-\zeta^2)^{1/2} \times \left[c + d\left(\frac{|\nabla n_\alpha|}{n_\alpha^{4/3}} + \frac{|\nabla n_\beta|}{n_\beta^{4/3}}\right) + r_s\right]^{-1} \mathrm{d}\mathbf{r}, \qquad (1)$$

where n_α, n_β are the spin electron density, and $n = n_\alpha + n_\beta$. The Wigner radius r_s is defined as $r_s = (3/4\pi n)^{1/3}$. The spin dependent factor ζ is defined as $\zeta = (n_\alpha - n_\beta)/(n_\alpha + n_\beta)$. a, b, c, d are coefficients determined by Wilson and Levy [12] after a minimization procedure. They minimized the quantity $(\partial E_c[n_\lambda]/\partial\lambda)_{\lambda=1}$ which should be near to zero for Hartree–Fock atomic densities. Their values are $a = -0.74860$, $b = 0.06001$, $c = 3.60073$, and $d = 0.90000$. In the fitting procedure only one experimental value, the correlation energy of the He atom, was used. Note that the functional vanishes for all one-electron densities, but so does it for completely spin-polarized systems with more than one electron. Because of the particular minimization procedure employed the value of the parameters could be dependent on the kind of densities used.

To calculate the correlation energy by means of the functional of eq. (1) Hartree–Fock densities are used. They were taken from the work of Merkle et al. [9] and only a short description is now given. The calculations were performed with good Gaussian basis sets (14s, 9p, 2d contracted to 7s, 5p, 2d excepting the cations C_2^+, N_2^+, O_2^+ and F_2^+) where the basis set was augmented to 14s, 9p, 3d, 2f contracted to 7s, 5p, 3d, 2f) at the experimental equilibrium distances. It is also possible to use the Hartree–Fock plus density functional equilibrium distances. However, Merkle et al. [9] estimated a deviation of less than 0.2 eV, which is below the errors of the density functionals. The behavior of the potential energy curves at large distances was not investigated. Improving the basis set did not change the results significantly [9]. The numerical integration scheme is related to that of Becke [13]. The integrand is first partitioned into atomic regions like Becke, and the angular integration is done, like Becke, following the works of Lebedev and Konyaev [14]. However, it differs in the radial integration which is done using the Patterson technique [15].

The ionization potentials are computed as the difference between the energies of the atoms or molecules and the ions at the equilibrium distance of the neutral molecule (adiabatic ionization potential). The dissociation energies are computed as the difference between the energies of the molecules and the atoms or ions. All experimental and Hartree–Fock values were taken from ref. [9].

Table 1
Ionization potentials (in eV)

System	HF [a]	HF+GGA91 [b]	HF+WL [c]	Exp. [d]
Li	5.34	5.53	5.39	5.39
Be	8.04	8.91	9.31	9.32
B	7.93	8.61	8.71	8.30
C	10.80	11.47	11.48	11.26
N	13.96	14.65	14.57	14.53
O	11.89	13.29	13.72	13.62
F	15.72	16.96	17.22	17.42
Li_2	4.27	5.00	5.52	5.15
Be_2	6.19	6.96	7.33	7.46
B_2	7.34	8.34	8.72	8.99
C_2	11.08	12.17	12.66	12.18
N_2	16.03	17.11	17.20	15.59
O_2	11.97	12.74	12.63	12.05
F_2	15.85	16.84	16.90	15.68
LiH	6.70	7.65	7.89	7.76
BeH	8.13	8.47	8.29	8.20
BH	8.45	9.42	9.75	9.76
CH	10.07	10.92	11.05	10.65
NH	12.78	13.58	13.55	13.51
OH	11.40	12.68	13.22	12.94
FH	14.41	15.55	15.72	16.10

[a] Hartree–Fock results [9].

[b] Hartree–Fock plus GGA91 [9].

[c] Hartree–Fock plus Wilson–Levy functional.

[d] Experimental values from ref. [9].

3. Results

The calculated ionization potentials are shown in table 1 and fig. 1. They are compared with the experimental values as well as with the results obtained with the GGA91 functional. The Hartree–Fock values are also given as a reference. In fig. 1 the calculated correlation contribution to ionization potentials are plotted and compared with the exact ones (for the same figures using the GGA91 functional, see ref. [9]).

The values of table 1 confirm the already well-established result that correlation energy functionals give a marked improvement over the Hartree–Fock values. The Wilson–Levy functional yields, in general, values slightly better than the GGA91 functional and it is surprisingly accurate for atoms. However, the main weaknesses of density functionals are still present. Marked deviations are shown for the dimers N_2, O_2 and F_2 (see fig. 1). Note that the exact correlation contribution to the ionization potential of N_2 and F_2 is negative. The average deviations of the GGA91 and Wilson–Levy functionals in calculating ionization potentials are 0.28 and 0.14 eV, for the atoms, 0.67 and 0.67 eV for the dimers, and 0.27 and 0.19 eV for the hydrides, respectively.

Tables 2 and 3 and fig. 2 show the results obtained for the dissociation energies. It is known that near-

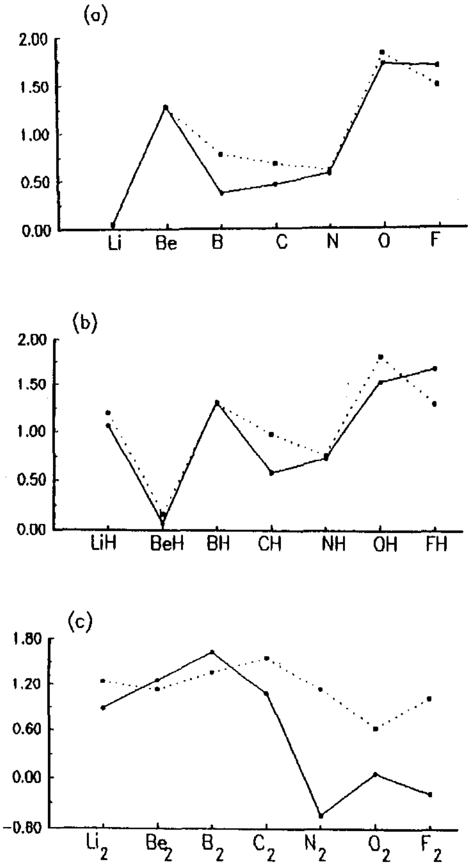

Fig. 1. Correlation contributions to ionization potentials (in eV) for (a) atoms, (b) hydrides and (c) dimers. Solid line: exact, dashed line: density functional.

Table 2
Dissociation energies (in eV)

System	HF [a]	HF+GGA91 [b]	HF+WL [c]	Exp. [d]
Li_2	0.16	0.76	1.37	1.06
Be_2	−0.33	−0.04	0.22	0.11
B_2	0.87	1.54	1.99	3.06
C_2	0.68	2.39	4.01	6.32
N_2	5.03	7.51	9.30	9.91
O_2	1.15	3.13	3.38	5.21
F_2	−1.37	−0.69	−0.41	1.66
Li_2^+	1.24	1.29	1.26	1.31
Be_2^+	1.52	1.91	2.20	1.97
B_2^+	1.47	1.81	1.99	2.25
C_2^+	0.40	1.70	2.81	5.38
N_2^+	3.15	5.05	8.63	8.85
O_2^+	1.29	3.13	4.47	6.78
F_2^+	−1.38	−0.56	−0.09	3.41
LiH	1.48	2.25	2.63	2.51
BeH	2.14	2.47	2.37	2.16
BH	2.78	3.47	3.75	3.56
CH	2.47	3.40	3.87	3.64
NH	2.09	3.21	3.69	3.63
OH	3.04	4.11	4.61	4.62
FH	4.34	5.35	5.70	6.12
LiH^+	0.12	0.13	0.13	0.12
BeH^+	2.06	2.93	3.39	3.28
BH^+	2.26	2.65	2.71	2.11
CH^+	3.19	3.95	4.29	4.25
NH^+	2.91	3.42	3.74	3.71
OH^+	5.22	5.29	4.97	5.28
FH^+	3.54	3.61	3.59	3.61

[a] Hartree–Fock results [9].
[b] Hartree–Fock plus GGA91 [9].
[c] Hartree–Fock plus Wilson–Levy functional.
[d] Experimental values from ref. [9].

Table 3
Dissociation energies. Comparison of various functionals (in eV)

	HF [a]	GGA91 [b]	B [c]	LYP [d]	WL [e]	Exp. [f]
Li_2	0.16	0.76	0.73	0.89	1.37	1.06
Be_2	−0.33	−0.04	−0.03	−0.19	0.22	0.11
B_2	0.87	1.54	1.58	1.36	1.99	3.06
C_2	0.68	2.39	2.39	2.34	4.01	6.32
N_2	5.03	7.51	7.45	7.67	9.30	9.91
O_2	1.15	3.13	2.84	2.67	3.38	5.21
F_2	−1.37	−0.69	−0.36	−0.53	−0.41	1.66

[a] Hartree–Fock.
[b] Hartree–Fock plus correlation energy calculated with the functional of Perdew [10,11].
[c] Hartree–Fock plus correlation energy calculated with the functional of Becke [16].
[d] Hartree–Fock plus correlation energy calculated with the functional of Lee, Yang and Parr [17].
[e] Hartree–Fock plus correlation energy calculated with the functional of Wilson and Levy [12].
[f] Experimental values [9].

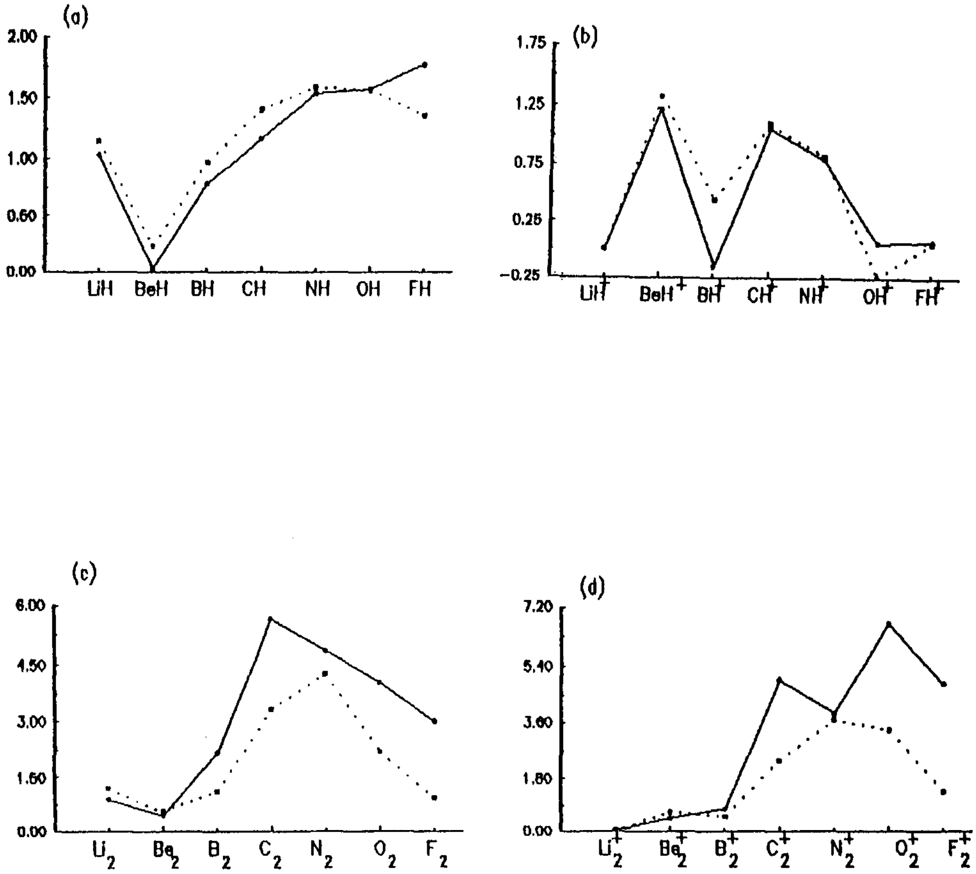

Fig. 2. Correlation contributions to dissociation energies (in eV) for (a) hydrides, (b) hydride cations, (c) dimers and (d) dimer cations.

degeneracy effects contribute markedly to the dissociation energy of the dimers and their cations causing enormous errors in the density functional calculations. The C_2 molecule is often cited as one of the worst cases with errors of more than 4 eV [8]. Therefore it is interesting to note that for this molecule the Wilson–Levy functional diminishes the deviation by almost 2 eV, and also gives a good improvement for the N_2 molecule. The same trend is found in the dissociation energies of the dimer cations, but it does not yield a positive binding energy for the F_2 molecule. However, one has to point out that F_2 remains a big challenge for every functional. The Wilson–Levy functional is the only one which binds the Be_2 molecule. The contributions to the dissociation energies of the hydrides and their cations are well reproduced as can be seen from fig. 2 and table 2. The average deviations of the GGA91 and Wilson–Levy functionals in calculating dissociation energies are 1.82 and 1.19 eV for the dimers, 2.23 and 1.31 eV for the dimer cations, 0.39 and 0.18 eV for the hydrides, and 0.21 and 0.16 eV for the hydrides cations, respectively. Finally, in table 3 the dissociation energies of the dimers calculated with various density functionals are compared. Confirming the already discussed values one can see that the dimer molecules are difficult cases for density functionals. Therefore, it is encouraging to see that the Wilson–Levy functional improves the result for almost all molecules.

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